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EDWARD HART, Editor, J. H. LONG, EDGAR F. SMITH.

COMMITTEE ON PAPERS AND PUBLICATIONS.

CONTENTS.

PAGE.

The Synthetic Food of the Future. By Harvey W. Wiley 155
The Determination of Phosphoric Acid. By H. Pemberton, Jr. 178
On the Estimation of Sulphur in Pyrites. By G. Lunge 181
Improvement in the Manufacture of Acetone. By E. R. Squibb 187
Report of Committee on Atomic Weights, Published During 1894. By F. W. Clarke 201
Coloring Matter in the California Red Wines. By W. D. Bigelow ... 213
The Penetration Machine—An Explanation. By H. C. Bowen 218
NOTES: Argon: A New Constituent of the Atmosphere; Calcium Sulphite Stalactites and Stalagmites 219
NEW BOOKS: A Text-Book of Inorganic Chemistry; Qualitative Chemical Analysis of Inorganic Substances as Practiced in Georgetown College 243

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PAPERS ACCEPTED FOR PUBLICATION:

Note on the Determination of Zinc. By P. W. Shimer.

The Separation of Solid and Liquid Fatty Acids. By E. Twitchell.

Some New Laboratory Apparatus. By Ewald Sauer.

A Cheap Form of Self-Regulating Gas Generator. By W. W. Andrews.

An Arrangement for Washing with Boiling Water. By Frank F. Jewett.

Some of the Properties of Calcium Carbide. By F. P. Venable and Thomas Clarke.

Issued with March Number, 1895.

Proceedings.

COUNCIL.

January 23, 1895, the following resolution was approved by a majority of the Council:

Resolved, That the salary of the Editor for the year 1895 be fixed at two hundred and fifty dollars ($250).

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MEETINGS OF THE SECTIONS.

CINCINNATI SECTION.

Discussion of paper by E. Twitchell, read January 15, 1895.

Dr. Newman asked Mr. Twitchell if he had ever mixed the pure solid and liquid fatty acids in the same proportion in which they were thought to exist in a given fat, and determined whether or not the iodine number of the mixture agreed with that of the fat.

Mr. Twitchell replied that he never had; he thought it was a good idea, but it was very difficult to obtain the liquid acids pure, and if obtained pure, on the slightest exposure to air, they would become more or less oxidized.

Replying to the question whether oleic acid could be obtained

pure, Mr. Twitchell said all fats contained linolic acid; he had never found a fat which contained oleic acid free from linolic.

Professor Lloyd stated that he had once tried this separation of solid and liquid fatty acid by Muter's method. His experience led him to believe that lead stearate and palmitate were soluble in the lead oleate, and this mixture was soluble in ether. While pure lead stearate and palmitate might be nearly or quite insoluble in ether, in the presence of the oleate, ether would dissolve an appreciable amount. He would like to know what Mr. Twitchell considered the so-called pure oleic acid of the market to be.

Mr. Twitchell replying, said it was probably oleic acid with some oxidized acids.

Professor Lloyd then asked whether any method by means of which ten per cent. of cottonseed-oil could be detected in olive-oil existed.

Mr. Twitchell replied that he would not be positive about ten per cent., thought possibly twenty per cent. could be detected; he said the difficulty was due to the fact that oils contain all the fatty acids in different proportions, that two samples of pure oil might vary as much as the mixtures, so far as chemical composition was concerned they were the same.

Mr. Smith remarked that Dr. Stuerke had carried on a series of experiments for over a year, and had found that he could not differentiate less than ten per cent. of oils. Artificial lards are made on this basis.

Mr. Twitchell said that by treating a sample of olive-oil known to be pure, and an adulterated oil with sulphuric acid of given strength, he thought, after some practice, one ought to be able to detect five per cent. of cottonseed-oil.

RHODE ISLAND SECTION.

The regular monthly meeting of the Section was held at Providence, January 17, 1895.

President Charles A. Catlin in the chair.

Mr. Geo. F. Andrews read a paper upon The Accuracy of the Fine Assay of Silver.

The paper briefly discussed the general inaccuracy of the fine assay of silver, and the difficulty of getting a satisfactorily accurate assay of ores by the methods now in use.

It also discussed, in some detail, the losses in cupelation due to absorption and to volatilization. The effect upon the button of too great heat and too large amount of lead.

Mr. E. D. Pearce gave an interesting account of the use of hydrocyanic acid in destroying insects upon trees.

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THE SYNTHETIC FOOD OF THE FUTURE.[1]

BY HARVEY W. WILEY.

THE problem of human nutrition is the great groundwork of sociology. I use the word nutrition in its broadest sense, including clothing and fuel, which, while not as essential as food to life, are quite as important factors in civilization. Until within a few years the study of nutrition and the means of providing it have been deemed the exclusive function of agriculture. In the development of this idea, we have seen springing into existence in all parts of the civilized world, within the past twenty-five years, colleges of agriculture and agronomic experiment stations in large numbers. Especially in this country have we seen the greatest activity in this line. In all the states and territories, fostered by the federal government, schools have been established in which instruction in agriculture has been made a fundamental branch of the college curriculum. There are fifty-seven agricultural experiment stations in the United States. Each state and territory has at least one. Louisiana has three, Alabama, Connecticut, Massachusetts, New Jersey, and New York each two, and the Department of Agriculture two, one in Florida and one in California. For the support of the state and territorial stations, Congress has made an appropriation for the fiscal year ending June 30th, 1895, of $745,000 and for the Department stations $10,000, in all $755,000. The agricultural colleges in the states and territories have also been endowed by

[1]Retiring Address of Harvey W. Wiley as President of the Society, Boylston Hall, Harvard University, Dec. 28, 1894.

grants of public land proportionate in extent to the numbers of senators and representatives in congress. The annual money value of these grants varies with their extent and the wisdom with which they have been invested, but the total sum is approximately a million and a half dollars. In addition to this a sum of money is granted annually to each agricultural college directly from the treasury, and this sum is to be increased at the rate of $1000 per annum until it amounts for each institution to $25,000 a year. This amount will be reached in five years. At present the total sum so granted is nearly a million dollars, and it will soon be a million and a quarter. The total amount of the financial aid thus granted directly from the treasury to the agricultural colleges and experiment stations is at the present time approximately three million and a quarter dollars annually. To this must be added the amount given directly by the states and arising from private endowments—a sum of no inconsiderable importance. In all it may be said that about four million dollars in this country are annually devoted to the promotion of agricultural and allied education and research, a sum more liberal than that devoted by any other country to similar objects.

The natural result from such investigations is an increase in soil productiveness, the reclamation of lands supposed heretofore to be unfit for tillage and a greater economy of food production. The supply of human food, therefore, appears to more than keep step with the increase in population and food consumption. In so far as economic reasons extend, there is no occasion to look outside of scientific agriculture for the supply of human food.

But another view is presented of the subject of a more strictly scientific aspect, based on the remarkable progress which has been made in the past few years in the domain of synthetic chemistry. The year 1828 marks a new era in the history of chemistry. It was in this year that Wöhler succeeded in making synthetic urea by the union of cyanic acid and ammonia. Urea is not of a high order of organic bodies; in fact, it is a result of retrograde action in the living organism and the consequent result of the breaking down of higher organic bodies; yet its artificial formation was a brilliant victory of chemical methods, a bold and successful charge

on the breastworks of organic compounds. To change the figure, it was the crossing of the dead line which had been drawn previously between the living cell and the inanimate crucible. The line once having been crossed, the old distinctions between the organic and the inorganic world have been completely obliterated. With them have gone also the divisions which were supposed to separate the animal from the plant. It is now known that animals do not get their entire nourishment from so-called organic nor plants from inorganic compounds. Many plants, especially those free of chlorophyl, live alone on organic compounds. Especially noteworthy among these, from the character of the chemical activity which they manifest, are the vegetations of a bacterial nature, living largely on organic products. Even the green plants first fabricate the inorganic elements into organic compounds before taking them into their tissues. The green cells are the tiny kitchens in which the meals of the plant molecules are prepared.

Without dwelling on further details of this subject, it is sufficient for the present purpose to state that the progress of modern science has entirely changed our ideas respecting the sharp lines of division which were formerly thought to exist between the animal and vegetable, and between the nature of artificial chemical compounds and those produced by biochemical action in the living organism. We stand, therefore, face to face with the fact that it is possible to produce, by artificial means in the laboratory, compounds which have heretofore been the results of exclusive biochemical functional activity of living organisms.

One remarkable fact in connection with Wöhler's synthesis of an organic compound is of interest here. While all the chemical world wondered at Wöhler's achievement, nearly fifty years elapsed before this rich field of chemical progress was further cultivated to any extent, with the single exception of the synthesis of acetic acid by Kolbe, in 1845. But since that time remarkable progress has been made. It is not my purpose here to recite in detail the synthetic accomplishments of Berthelot, Kekulé, Kolbe, Maumené, Baeyer, Hoffmann, Frankland, Ladenberg, Fischer, and many other celebrated workers in this field.[1]

[1] See Rise and Development of Organic Chemistry, by C. Schorlemmer, revised edition, 1894.

For the purpose of the present paper, only two points in organic chemical synthesis need be considered; *viz.*, first, the economy of the process, and second, the probability of the production of food compounds suited to the nourishment of man.

In respect of the first point, we find many illustrative examples of synthetic products which are furnished at so small an expense as to practically exclude from the market the corresponding natural articles. Among these may be mentioned salicylic acid made artificially by Kolbe's[1] process. Salicylic acid occurs as a natural product in the flowers of *Spirea ulmaria* and as a methyl ether in the oil of wintergreen (*Gaultheria procumbens*). It can be formed by synthesis in various ways, as, for instance, by fusion of salicylaldehyde with potassium hydroxide. Salicine, coumarine, indigo, cresol, or toluenesulphonic acid may be substituted for the salicylaldehyde. When phenyl carbonate is heated with a caustic alkali, salicylic acid is also produced. It may also be obtained when an alkaline solution of phenol is boiled with carbon tetrachloride. But none of these processes, although of great interest chemically, have any value commercially save that of Kolbe, or more properly, Kolbe and Lautemann, which consists of passing carbon dioxide into sodium phenylate.

But it will be observed that the phenol which is the base of the process, is itself an organic compound, or the result of the destructive distillation of an organic compound produced by nature. It is not impossible to produce phenol by artificial synthesis. It is said that by surrounding the points of an electric arc light with hydrogen that carbon and hydrogen combine to form acetylene, C_2H_2. According to Berthelot,[2] fuming sulfuric acid absorbs acetylene and the product so formed fused with caustic soda forms phenol or sodium phenate. But it needs no further illustration to show that a phenol formed in this manner could never, on account of its great cost, be used for the commercial manufacture of salicylic acid.

A distinction should be made in this matter between the formation of possible food products by synthesis from existing organic natural bodies, and the synthesis which begins with the inorganic elements themselves. The transformation of one organic

[1] *J. prakt. Chem.*, **2**, 10, 93.
[2] *Compt. rend.*, **68**, 539.

body into another of greater value to human industry is quite a different matter from the building up of organic bodies without the help of a living organism. Berthelot himself, who is now the apostle of synthetic foods, summarizes the steps which will probably be traversed on the way which is to end in the substitution of the chemist for the farmer:

1. Hydrocarbons, obtained by the union of hydrogen and carbon.
2. Alcohols formed from the hydrocarbons in various ways.
3. Aldehydes and acids obtained from alcohol by oxidation.
4. Amides produced by the action of ammonia on the alcohols.
5. Alkaloids formed by the action of ammonia on the alcohols and aldehydes.

But even granting the fullest development of such a scheme, the impartial observer will be compelled to admit that there is still an immense gulf between the best of the products formed and human food.

In the case of medicines and drugs, perhaps the case is more hopeful. In so far as mere transformation of one organic substance into another of greater therapeutic value is concerned, much progress has already been made. But in nearly all of these cases the products are obtained by the splitting up of more complex into less complex molecules. In other words, it is a retrograde synthesis and not a constructive one. A mere list of remedies in common use, which have been formed in this way, would form an extensive index of pharmacy.

Both Liebig and Wöhler, as early as 1837, foresaw this advance in synthetic chemistry and predicted the synthesis of alkaloids and antiseptics and even of sugar.

Founded on the classical researches of Williamson on etherification has been built the art of forming by synthesis a great variety of flavoring matters for food and drink. In the strict sense of the term, these condiments are not foods inasmuch as they are not subject to digestion and do not take any part in the nourishment of the tissues. They have a nearer relationship, however, to the purpose of this address than the bodies already mentioned.

The slow natural oxidation of the alcohols in fermented and dis-

tilled drinks, giving rise to ethers of delicate odor and flavor, is an expensive process, and synthetic chemistry has boldly come to the aid of nature. The essences of fruits and flowers are now elaborated in great numbers in our laboratories and supply to a certain extent the natural products. With the aid of ethyl alcohol, burnt sugar, and a collection of artificial essences, the skillful manipulator will mix, in short order, drinks which resemble bourbon and old rye, madeira and sherry. The pure fruit flavors of many soda-water fountains could easily prove an alibi in respect of orchards. In the great majority of cases these essences are also the products of retrograde synthesis, or have for the base of manufacture an alcohol derived from the fermentation of a natural sugar. While it is true that they can be manufactured at a lower cost than attends their natural production, and while they are used as condiments in foods and drinks, yet in no sense can they be regarded as a step toward the preparation of foods from inorganic elements by purely chemical means. The principal artificial flavoring extracts are the derivatives of the fatty acids, especially the ethers and aldehydes. The ethereal salts of acetic, valerianic, benzoic, salicylic, and butyric acids, are the most common of these bodies. Methyl, ethyl, and amyl are the bases most usually found in the above compounds. Vanillin has also been made synthetically. Analysis showed that this natural product of the vanilla fruit was methylprotocatechuic aldehyde. This knowledge led to its artificial production. From turpentine is derived a perfume turpineol which is known as "lily of the valley." The artificial production of musk and of the perfume of the violet have also been accomplished.

Whether or not these bodies are injurious to health is a question whose discussion can not be entered into here. In the case of one of the best known of these condiments, and one which is not of ethereal origin, it may be said that its use in foods is prohibited in some countries, whether it be used as a sweetener or as an antiseptic. In justice to saccharin, however, it should be stated that repressive legislation against it has been quite as much due to a feeling of jealousy on the part of beet-sugar producers as to a suspicion of unwholesomeness on the part of the medical fraternity. Certain it is, however, that, even as a sweet-

ener, it will never take the place of sugar and because of its antiseptic properties it must necessarily interfere to some degree with the action of the digestive ferments.

It is not necessary to take up in detail other synthetic compounds which have attained a commercial success. The artificial dye stuffs are types of these bodies and illustrate, in a most brilliant manner, the progress of chemical synthesis based on the knowledge of the internal constitution of organic compounds derived from analytical investigations. But even the most enthusiastic believer in the future triumphs of chemical science will fail to find anything more than an inspiration in these achievements in respect of the production of foods. In all cases of coloring matters, original organic compounds derived from living cells, or the products of their destruction, have served as the bases of the processes. Without an elaborate review of this field therefore, and which, moreover, has already been made,[1] we pass at once to consider these achievements in synthesis which relate directly to the matter under consideration.

Along two lines of especial interest to food production, synthetic chemistry has made its greatest advances; *viz.*, the production of glycerides and of sugars. Wurtz[2] has described a method of synthesizing glycerol, which, in logic, would be called arguing in a circle.

Tribromhydrine, $\begin{matrix} HCHBr \\ CHBr \\ HCHBr \end{matrix}$, is decomposed with silver acetate forming triacetine. This is saponified by baryta yielding glycerol. The tribromhydrine, however, is first prepared from glycerol or rather from allyl iodide made from glycerol. At the end of this long synthesis, therefore, the chemist is exactly on the spot whence he started. Friedel and Silva[3], however, made glycerol in a different way. Trichlorhydrine is prepared from propylene chloride and saponified by heating with water. The propylene used is made from acetone. Wagner[4] produced glycerol by oxidizing allyl alcohol with potassium permanganate.

[1] *Ber d. chem. Ges.*, *1891*, **24**, 1007.
[2] *Ann. Chem.* (Liebig), **102**, 339.
[3] *Bull. Soc. Chim.*, **20**, 98.
[4] *Ber d. chem. Ges.*, **21**, 3351.

Glycerol has also been formed synthetically by other investigators, but the principles involved are not greatly different from those set forth.

The first notice I have seen of the artificial formation of a fat is in a paper by Pelouze and Gelis[1] published in 1844. It is said that by gently heating a mixture of glycerol, butyric acid, and strong sulphuric acid, and afterwards diluting with water a yellowish oil separates. This fat is not soluble, or only slightly so, in water. It is soluble in all proportions in strong alcohol and in ether. Caustic potash breaks it up into butyric acid and glycerol. It may be formed at ordinary temperatures by passing a current of hydrochloric acid into a mixture of butyric acid and glycerol and afterwards diluting. The authors thought this body to be the butyrine discovered in butter by Chevreul. Its great solubility in alcohol would lead us in this day to suppose that the body was not a true butyrine.

Our present knowledge of the natural fats is based almost solely on the classic researches of Chevreul. While the work of Chevreul was purely analytic in its character, the knowledge of the constitution of fats which it disseminated has been the foundation on which all subsequent structures have been built. While at the present day chemists do not recognize the existence of margaric acid and margarine, all the other fatty bodies described by Chevreul have been found to have substantially the constitution which he assigned them.

Berthelot's first important contribution to the synthesis of fats was presented to the French Academy of Sciences on the 5th of September, 1853. It was entitled "Memoire sur les combinaisons de la glycerine avec les acides et sur la synthese des principes immediats des graisses des animaux."[2] From Berthelot's paper we learn that glycerol was discovered in 1779 by Scheele[3] in making lead plaster.

Fourcroy was the first to theorize on the nature of fats[4].

Berthelot regarded the formation of soap as due to the affinity of oils for alkali.[5]

[1] *Ann. chim. phys.*, *1844*, [3], **10**, 434.
[2] *Ann. chim. phys.*, *1854*, [3], **41**, 216.
[3] *Opuscula*, **2**, 175.
[4] *Systeme des connaissances chimiques*, **7**, 142, 323, 329, and 334.
[5] Chevreul, *Ann. chim. phys.*, **88**, 226.

Fourcroy in his work on the fat of cadavers, substituted another idea for this rational one, thinking the formation of soap due to the oxidation of the oil under the influence of alkali and air. He classed the vegetable oils, waxes, cadaveric fats, fats liberated from soaps by acid, cholesterine, etc., together under the name "adipocere."[1]

In 1815, simultaneously with the discoveries of Chevreul, Braconnot rejected the ideas of Fourcroy, saying:

"When tallow is agitated with acid or alkali, the three constituents, hydrogen, oxygen, and carbon, which had been in a state of equilibrium, separate and rearrange themselves in another order, giving rise to adipocere and to a very fusible fat, soluble in alcohol.[2]

Pelouze produced sulphoglyceric acids and phosphoglyceric acids and together with Gelis[3] he made butyrine, the first artificially prepared fat.

Berthelot has generalized this work by combining glycerol with both organic and inorganic acids. The bodies produced are, as a rule, neutral and incapable of directly uniting with alkali. Some reproduce the natural fats.

Stearins.—Stearic acid, melting at 70° and prepared according to the method of Chevreul,[4] forms with glycerol three neutral bodies, mono-, di-, and tristearin. The last is identical with natural stearin. To make monostearin; Berthelot heats equal parts of glycerol and stearic acid to 200° for thirty-six hours in a sealed tube. The body formed is insoluble in glycerol and readily separates from the excess of this body. It may be purified by heating to 100° with ether and quicklime to deprive it of excess of stearic acid.

To make distearin: This body may be formed by heating equal parts of glycerol and stearic acid to 100° for 114 hours, or to 275° for seven hours. It may also be formed by heating natural stearin to 200° for twenty-hours in the presence of glycerol. Another method is to heat monostearin to 260° for three

[1] *Ann. chim. phys.*, 3, 129; Ibid, 5, 154; Ibid, 8, 17, 23, 31, and 67.

[2] *Ann. chim. phys.*, 93, 271.

[3] Sur la acide sulfoglycerique, *Compt. rend.*, 21, 718; Sur la butyrine, Nouvelles, *Ann chim phys.*, 10, 455.

[4] Recherches sur les corps gras, page 206.

hours in the presence of three parts of stearic acid. However formed, it is to be purified by the treatment with ether and lime.

To make tristearin: This body is obtained by heating monostearin to 270° for three hours with fifteen or twenty times its weight of stearic acid. Water is eliminated. The product is to be purified with ether and lime. The properties of natural and artificial stearin coincide as nearly as can be expected, considering the fact that natural stearin is never obtained pure. The nearest approach in properties by natural stearin to those of the artificial, was that shown by a preparation made by P. Duffy[1] who purified it by thirty-two crystallizations. The acid prepared by saponification, etc., from the synthetic stearin had the same melting-point as that originally employed.

Margarines.—Margaric acid from human fat[2] forms two neutral combinations with glycerol, monomargarine, and trimargarine.

To make monomargarine: Monomargarine may be prepared by heating a mixture of glycerol and margaric acid to 200° for twenty-one hours or to 100° for 106 hours. The reaction takes place with great readiness, in fact the synthesis is easier than that of any other fat. The same body or a similar one, is formed by simple contact of the constituents at ordinary temperatures for three months, though in very small quantity. A margarine is also formed by heating a mixture of margaric acid and glycerol saturated with hydrochloric acid, to 100° for some hours, but it is always contaminated with chlorhydrine.

Trimargarine is formed by heating monomargarine to 270° for seven hours in the presence of excess of margaric acid. The fat acid separated from it by saponification, etc., had the same melting-point as that originally employed.

Palmitins.—Three palmitins were formed in the way employed for the preceding fats.

Oleins.—Three were formed. The oleic acid employed was purified by the method suggested by Gottliebe.[3] The commercial acid was twice chilled and filtered and then converted into a potash soap. The soap was dissolved in twice its weight of alco-

[1] *Quart. Jour. Chem. Soc.*, Jan., *1853*, pages 303, 309, 310.
[2] Chevreul, Recherches, sur les corps gras, page 59.
[3] *Ann. der Chem. u. Pharm.*, 57, 93.

hol, filtered cold, and precipitated with barium chloride. The barium soap was recrystallized from boiling alcohol (one liter of strong alcohol dissolves five grams), and then decomposed by tartaric acid in an atmosphere of hydrogen.

Valerines, butyrines and acetines were formed in the same general manner.

All these fats could also be produced, and more easily, by heating the components to 100° in the presence of an auxiliary acid, such as sulphuric, hydrochloric, tartaric, phosphoric, etc. Triacetine has also been formed by Böttenger[1] by the action of acetic anhydride on glycerol in the presence of acid potassium sulphate.

In this direction the work of molecule building has been carried a step further in securing the construction of a higher glyceride containing phosphorus. Hundeshagen[2] has succeeded in preparing a substance similar to lecithin, which is one of the essential constituents of cell plasma. In this work he followed first in the steps of Berthelot in securing distearin (distearylglycerol) by heating stearic acid with an equal volume of anhydrous glycerol for thirty hours in closed tubes at 200°. The purified distearin, heated to 110° with metaphosphoric acid or phosphoric anhydride, gave the desired phosphorus compound. Numbers of the salts and derivatives of the distearylglycerol phosphoric acid have also been prepared and studied.

In the matter of sugars greater progress has been made. The elder Thenard, more than fifty years ago, proposed a scheme for the direct production of sucrose by the condensation of carbon dioxide, water, and ethylene. Kiliani, Tollens, and many others have made important contributions to this work, but by far the most important advances in the synthesis of sugars have been made by Fischer. His work has been most thoroughly reviewed in this country by Keiser[3] and Stone.[4] Fischer[5] has also published a résumé of his work. Starting with formaldehyde and passing through glycerol and acrolein, Fischer, by a series of beautifully conceived researches, has succeeded in forming,

[1] *Ann. Chem.*, **263**, 359.
[2] *J. prakt. Chem.*, neue Folge, **28**, 219.
[3] *Am. Chem. J.*, **11**, 277, and **12**, 357.
[4] *Ag. Science*, **6**, 166.
[5] *Ber d. chem. Ges.*, **23**, 2114, and **27**, 3189.

by synthesis, a large number of sugars, some of which have not been discovered in nature. For the details of this work, the reviews mentioned can be consulted.

Lately in the same direction, another step has been taken. Fischer and Bunsch[1] have shown that the sugars under the influence of hydrochloric acid in the presence of alcohols and oxyacids are condensed to polysaccharides resembling glucosides.[2] Of these bodies methyl glucoside, $C_6H_6O_{11}CH_3$, methyl arabinoside, $C_5H_9O_5CH_3$, ethylarabinoside, $C_5H_9O_5C_2H_5$, ethylglucoside, $C_6H_{11}O_6C_2H_5$, methylgalactoside, $C_6H_{11}O_6CH_3$, ethylgalactoside, $C_6H_{11}O_6C_2H_5$ and benzylarabinoside, $C_5H_9O_5$, CH_2, C_6H_5 have already been formed.

Previous to the appearance of the above papers, Michael[3] had described a method for the synthesis of a glucoside. This method depends on the interaction taking place between so-called acetochlorhydrose and the alkaline carbolates. The method yields only a moderate product and is somewhat troublesome.

The process employed by Fischer in converting sugars into glucosidal bodies is well illustrated by the following example:

Grape sugar is dissolved in methyl alcohol and in the cold the solution is saturated with gaseous hydrochloric acid. The solution soon loses its power to reduce alkaline copper under this treatment and a crystalline product is formed. The reaction which takes place is represented by the following formula:

$$C_6H_{12}O_6 + CH_3OH = C_6H_{11}O_6CH_3 + H_2O.$$

To this substance the name methyl glucoside is given. The other bodies named above are formed by similar reactions.

Fischer, however, freely admits that although synthesis has done so much in the way of producing compounds which heretofore have been deemed the exclusive product of living vegetable cells, yet in the case of sugars an essential difference still exists.[4] In the laboratory there is produced at first only an inactive sugar which afterwards, by means of special operations, is split up into the active modifications, while the assimilation

[1] *Ber d. chem. Ges.*, **27**, 2478.

[2] *Ber d. chem. Ges.*, **26**, 2400.

[3] *Compt. rend.*, **89**, 355.

[4] Oration before the Institute for Military Surgeons, August 2, 1894, Neue Zeitschrift für Rübenzucker-Industrie, **23**, 185.

process of plants gives directly the active sugars of the same geometrical series. The stereochemistry of the carbohydrates, however, furnishes for this fact a full explanation.

If, in the case of an active sugar, by means of hydrocyanic acid, an additional carbon atom is added, the artificial process takes place in an asymmetric way. Since now in plant assimilation the optically active constituents of the chlorophyl granule take part in the production of carbohydrates, it is easy to understand how from the beginning, the formation of sugars with six carbon atoms takes place in an asymmetric manner.

In so far as I have been able to determine, no experiments have been made to determine the digestive coefficient of these synthetic foods. In the case of the artificial sugars many of them are unaffected by alcoholic ferments and it is safe to assume that the digestive ferments would be equally powerless to disintegrate them. The direct products of sugar synthesis are, as a rule, neutral to polarized light. This does not imply that morphologically they are so different from the natural products, but rather that the carbon asymmetry is inversely twinned and the product is composed of equal quantities of right and left-handed sugars.

Of the natural sugars, levulose is the only left-handed one of any economic or digestive importance. The specific rotatory power of this body varies with the temperature, and at 88° the disjointed carbon atoms are so much reduced in position as to show a rotatory power equal to that of dextrose.

So far, it does not appear that the left-handed sugars made by synthesis have all the properties of levulose. They seem to be somewhat different in their stereometric relations from the natural product. In fact, the theory does not require that the left-handed sugars be levulose, but that they be simply the twin asymmetric duplicates of the right-handed varieties. Left-handed dextrose, therefore, is an entirely different substance from levulose. For the old name dextrose, Fischer uses glucose, and for levulose, fructose. The prefixes l., d., and i., signify left and right polarizing and inactive respectively. In one case, however, he has discovered a. d. fructose as well as a. l. glucose

We have seen how by slow and painful steps and by round-

about ways the synthesis of sugar has gradually progressed until products containing nine molecules of carbon have been obtained. The ordinary sugar of commerce, saccharose, contains a molecule with twelve atoms of carbon. This sugar, however, can not be strictly considered as a dodekose, for it appears to be the product of the condensation of two hexoses. Whatever may be the true theory of its composition, whether wholly of the aldehyde type or a hybrid aldehyde ketone, yet its structure is of a higher order than the simple hexoses and it has not been formed artificially by any of the usual processes of synthesis.

It has remained for an inventor to take a short cut across the synthetic field and make saccharose *per saltum*.

Jean Ercole Pelligrini, a citizen of Italy, residing in France, has taken out a patent in this country for making sugar in a thoroughly direct manner. Ethylene gas, carbon dioxide, and steam are admitted in proper porportions to a channeled cube of pumice stone, impregnated with platinum sponge. The carbon dioxide and ethylene are used in practically equal volumes and the steam *ad libitum*. The pressure is so regulated that each gas will gradually diffuse through the whole porous platinized space. The operation is continued for about half an hour and "at the end of this period" to quote the language of the letters patent, "a sirup containing from twenty to twenty-five per cent. of sugar is withdrawn."

A sample of the sirup submitted with the application for the patent was examined in the laboratory of the Division of Chemistry at Washington and found to be sucrose. That it was made in the manner described, however, is a matter which, to my mind, requires further demonstration. The examiners of the Patent Office were, nevertheless, assured of the genuineness of the sample, by what proof I know not. For my part, I do not believe that a single molecule of sucrose can be made by that process. Some simple organic acid might be produced in this way, possibly some inactive sugar, but where shall we look for the stereochemical asymmetry which is so predominant a feature in that complex molecule which we call saccharose?

But for the sake of argument, grant the actual production of this substance. The price of a pound of carbon dioxide is far

greater than that of a pound of sugar, and ethylene is still far more expensive. If the process of Pelligrini really works as well as the United States has certified, the sugar would cost nearly a dollar a pound. The whole process, in my opinion, may be classed with the electrical refining methods so successfully employed a few years ago in scientific buncoing. A full exposition of the fallacies of the method is given by Maumené.[1]

In the foregoing pages I have attempted to give a synopsis of some of the forms of organic synthesis which would enable us to come to a definite opinion regarding the possible production of artificial food. The prospect, it must be admitted, is not a flattering one.

First of all, it is seen that all cases of successful synthesis from an economic sense, belong either to the class already mentioned, *viz.*, retrograde synthesis, or to a process depending on the use of already existing organic compounds.

In this direction chemistry has a wealth of future achievements to offer commerce. The changes and modifications which can be made in natural products will continue hereafter, as in the past, to present to chemical science problems of the most promising success. As in the case of the polysaccharide starch, from which a simple hexose sugar is produced of the widest use in the arts, so with other organic products of the field, many victories in retrograde synthesis may be won. Chemistry will show how to make many foods more useful, and in the way of cooking more nutritious and palatable. In respect of the direct or indirect union of the elements into successful food products, there is not a single instance in all that have been cited to give any hope whatever.

In the way of economy the simple synthesis of hydrogen and nitrogen to form ammonia has never seen any chance of economic success. Here in one way, at least, synthesis might help to increase the stores of food. Nitrogen in ammonia salts is now worth eighteen cents a pound to the farmer. A simple synthesis would materially reduce its price. It might be well for the ambitious chemist to begin with ammonia before attempting albumen. While the scientific difficulties are less formidable

[1] *Jour. de Fab. de Sucre*, 35, No. 4.

than the economic ones, yet they are apparently unsurmountable. A single pound of synthetic sugar must be worth many dollars, and we do not know that it will submit itself to digestion. The complex molecules of albuminoids and starches seem to me to be beyond the reach of chemical handicraft. There is no possibility of making many of the nutritive constituents of porterhouse steak, much less the mixing of them into an attractive and tempting form. In the field of scientific research, however, and the light which will be thrown on molecular structure, there are no limits to the triumphs of synthetic chemistry.

As the periodic law among the elements, so the theories of stereostructure, isomerism, asymmetry, and condensation have led and will lead to the greatest discoveries. When the investigator is once convinced of the possibility of any compound he will never cease to look for it until its discovery crowns his efforts. As the disturbance caused by an unknown body in space leads the astronomer to train his glass on the unexplored depths of the heavens, so do the missing links in molecular structures incite the chemist to renewed exertions. This fact is beautifully illustrated in the case of the carbohydrates. In the last few years there have been added to the number of sugars known to be produced by nature, more than twenty built by synthesis. But large numbers of possible sugars are still missing.

According to Fischer,[1] every asymmetric carbon atom in a carbohydrate molecule makes two forms possible. There can, therefore, be at least eight hexoses, and each of these is optically paired, making sixteen in all. Ten years ago only two of like structure of this number were known. Now ten have been discovered, and six yet remain unknown. Of the pentoses there are eight possible forms, of which four have been discovered. Of the thirty-two possible heptoses, only six are known, and of the 128 nonoses, only two. Since the possible number of compounds increases in a geometrical ratio with the addition of carbon atoms, it is seen that the field for discovery is not soon likely to be exhausted. But the molecule builder, it seems certain, must take his stones from Nature's quarries. He may fashion and change them, adapt them to new uses and endow them with more

[1] Neue Zeitschrift für Rübenzucker-Industrie, 23, 169.

valuable properties, but he can not make them of the raw original materials.

Schorlemmer in the revised edition of his Development of Organic Chemistry, while taking a very sanguine view of the future progress of synthetic chemistry, does not expect it to interfere with the farmer. He expects, at most, morphia and quinia to come from the laboratory instead of from the poppy and cinchona.

Roscoe says: "But now the question may be put, is any limit set to this synthetic power of the chemist? Although the danger of dogmatism, as to the progress of science, has already been shown in too many instances, yet one can not help feeling that the barrier which exists between the organized and unorganized world is one which the chemist at present sees no chance of breaking down.

It is true that there are those who profess to foresee the day when the chemist by a succession of constructive efforts, may pass beyond albumen and gather the elements of lifeless matter into a living structure. Whatever may be said regarding this from other standpoints the chemist can only say that at present no such problem lies within his province. Protoplasm with which the simplest manifestations of life are associated is not a compound but a structure built up of compounds. The chemist may successfully synthesize any of its component molecules, but he has no more reason to expect the synthetic production of the structure than to imagine that the synthesis of gallic acid leads to the artificial production of nutgalls."[1]

It seems strange, therefore, that one of the most eminent of living chemists should have so unequivocally committed himself to the doctrine of future synthetic foods.

In an address before the Society of Chemical and Mechanical Industries in Paris, on the 5th of April, 1894, Berthelot publicly proclaimed his theory of the coming suppression of agriculture and the substitution of synthetic foods for its products. This theory he has more fully elaborated in McClure's Magazine for September 1894. The accomplishments in synthetic chemistry on which he bases his predictions are essentially those which

[1] Presidential Address, British Association, *Chem. News*, Sept. 2, *1887*, p. 100.

have been set forth already in this address. With proverbial European provincialism, however, he fails to mention one of the strongest of the arguments he might have used; *viz.*, Fischer's sugar synthesis. The wildcat process lately patented in this country, however, as well as in France, for making sugar by the condensation of ethylene receives favorable mention and no doubt is entertained of the speedy manufacture of sugar on the largest scale synthetically and that the culture of the sugar-beet and sugar-cane will be abandoned because they will have ceased to pay. The struggling sugar planters of our own country who during the present season have been making sugar at a cost of four cents a pound and selling it for three, will bear witness to the fact that this happy period has already arrived.

The synthesis of the dyestuffs, especially of alizarin and indigo, he cites as examples of the destruction of an agricultural industry by chemical achievements. He dwells, and very properly, on his own work in the synthesis of fats as evidence of what may be accomplished in that line. The beefsteak of the future may not be identical with that of to-day, but it will be a tablet of any color or shape desired and will entirely satisfy the epicurean senses of the year 2000. Chemistry has developed the whole science of cookery and flavoring and provided all the utensils of the kitchen. It remains now only for it to complete its work and furnish the food itself. Even at the present time, according to Berthelot, tea and coffee could be made artificially if the necessity should arise. The caffeine of the chemist has the following genealogy:

Carbon and oxygen beget carbon dioxide.

Carbon dioxide and chlorine beget carbonyl chloride.

Carbonyl chloride and ammonia beget urea.

From urea comes uric acid.

From uric acid is derived xanthin.

Xanthin yields theobromine.

Theobromine yields theine or caffeine.

From this pedigree it is concluded that tea plants, and cocoa and coffee trees will soon follow the madder and indigo plants into economic eclipse. No attempt is made to compute the cost of the caffeine necessary for a single cup of Java; and the fact that caffeine is only one of its constituents is naïvely ignored.

Tobacco also is soon to follow because something resembling nicotine has already been made synthetically. While nicotine has not yet been made synthetically, its near relationship to conine, the active principle of hemlock, which has been so formed, leaves little doubt of the speedy accomplishment of this desirable end.

In regard to the synthesis of food products directly from the elements attention is called to the following points:

By means of the electric spark acting on hydrogen and carbon at a white heat, acetylene is produced.

Acetylene will combine with another atom of nascent hydrogen forming ethylene and marsh-gas.

Ethylene can be made to combine with the elements of water forming common alcohol, while marsh-gas in similar circumstances, yields methyl alcohol.

Acetylene with nascent oxygen forms oxalic acid.

Acetylene in contact with nitrogen subjected to the electric spark forms hydrocyanic acid.

Acetylene and oxygen in the presence of water and an alkali form an acetate, whence acetic acid.

"I also found," says Berthelot, "that ethylene under certain conditions could be transformed directly into benzene. Here then we have seven familiar compounds of wide utility; acetylene, marsh-gas, alcohol, oxalic acid, acetic acid, cyanhydric acid, and benzene, to say nothing of many others which I might mention obtained from these elements direct. Now imagine for a moment the enormous number of organic compounds into the constitution of which, according to regularly acting laws, these seven different compounds enter. There are six different families of alcohols alone and each one of these families embraces a greater or less number of special alcohols. Over the whole field of organic chemistry the mystery of possibilities extends. Its combinations and intercombinations are so limitless that we can only work on regularly to ends that it is impossible to foresee."

According to Berthelot, the fields which are now defaced by agriculture will be beautified by regaining their natural covering and the earth will be one vast park of pleasure and the chemist the great conservator of the human race.

A synthetic climate will replace the capricious one furnished by nature. Winds and waterfalls will provide power and light, and the bowels of the earth, tapped by frequent wells to a great depth, will supply the superheated steam to turn the winter into spring and to bring together the pole and the equator. When these predictions are read we first think that Bellamy has turned chemist, and by reincarnation in the shape of the great Parisian Savant has thrust upon the scientific world a new edition of "Looking Backwards."

In all the instances brought forth there is not the slightest approach to anything to justify the prophecy of a period of artificial food. The few cases of synthesis in which the products approach the composition of anything digestible present such insurmountable difficulties in expense and supervision as to render any expectation of reaching economic results utterly futile. In the great majority of cases, as has been seen, the process of synthesis is conducted on materials already organized by living cells. The enormous cost of building up any kind of a commercial, synthetic organic body directly from the elements is such as to render it, in my opinion, utterly improbable of successful achievement.

Even if food products can be formed in the crucible there is no reason whatever for supposing that they can ever play any rôle in an economic sense. The untold billions of laboratories which nature builds are infinitely cheaper in construction and operation than those filled with platinum and porcelain. The sun ignites the crucibles of nature at an expense far less than attends the use of the city gas works. The director of Nature's laboratory depends on no endowment nor legislation for his salary and his bills for supplies are not disallowed by any board of auditors on the score of economy. Night and day his patient faithful assistants work without thirst for fame, without hope of reward. They fight not for priority of discovery and their anonymous papers are printed in rich profusion in the great Berichte of the universe. The chemistry of the chlorophyl cell is far more wonderful than any of the achievements of Lavoisier, Berzelius, or Fischer.

It would doubtless be a solace to the weary toiler in the sun to

look forward to a time when he might lie in the shade while proteids were pricking up their ears in the condenser and fats frying in the scientific pan. But in the days of the far future, while Berthelot will still be honored and Fischer praised, the farmer will be found following in the furrow, fields of waving grain will brighten the landscape, and herds of kine graze upon the hills.

Members of the Society:

According to the provisions of our Constitution, the time has arrived when I am to take my leave of you as President of the Society. I thank you most heartily for the honor twice conferred upon me of presiding over this great organization. It is only fitting at this moment that I should give a brief account of my stewardship.

One of the most gratifying features in connection with the history of the Society during the past two years, is the increase in membership. In two years, according to the data furnished by the Secretary, the Society has more than doubled its membership. Our membership now is well up to the thousand mark. I should have been better pleased at this time to take leave of a membership of fully 1,000, but I feel sure that this number will soon be reached.

The JOURNAL of the Society has fully kept pace with the increase of membership. The volume for 1893 contains 720 pages, devoted almost exclusively to original articles, of which 98 appeared. The volume for 1894 contains 891 pages, exclusive of proceedings, and 158 original articles. In addition to the copies furnished the members of the Society, there is a large number of subscribers to the journal in this and foreign countries, so that the total circulation at the present time is over 1,000. It is recognized as a leading chemical journal by the editors of foreign periodicals. More than thirty of its articles, during the past year, have been reprinted wholly or in part in the *Chemical News*, and a large number of abstracts has appeared in the *Journal of the English Society*, the *Berichte*, and the *Central-Blatt*, in which, during the past twelve months, over 100 abstracts of articles from the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY have appeared. These are figures which are very gratifying to us all.

The prosperity of the Society has been due to united action among all its members, and a determination to make it a success.

Local Sections have been established during the past two years in Washington, the Lehigh Valley, and in New Orleans. The chemists of the Pacific Slope have also expressed a desire to unite with the Society at an early date and establish a Local Section. There are many other places where the membership of the Society would justify the establishment of Local Sections, and especially is this true of Baltimore, Philadelphia, Boston, Cleveland, and Chicago, and it is hoped that speedy action may be taken to secure these desirable results.

To the editor and the Committee on Publications the Society is indebted for energetic and systematic work in increasing the efficiency of the JOURNAL, but the efforts which these gentlemen have made would have had but little success had not the members of the Society throughout all parts of the country come forward with contributions of papers. There are often good reasons why a paper on any particular subject should be published in a particular journal in this or other countries, but as a rule it seems to me that American authors should first offer their papers to American journals, and if this rule is followed it is certain that the journal of our own Society will receive a fair share of the contributions. We would not desire to exclude from the field any other journal, but we are justified in asking that due consideration be given our own journal by our members in the distribution of their papers.

The American Chemical Society represents American chemical science as a whole and therefore it is desirable that the journal of the Society should not become the organ of any particular branch of chemical science. The editor and the Committee on Publications have kept this end in view in the distribution of the articles and have endeavored to put into each number something of interest to many of the special departments of chemical science. Our doors are open for the entrance of those engaged in didactic chemistry, for organic chemists, for technical chemists, for agricultural chemists, for mining and assaying chemists, for general manufacturing chemists, and in fact for every branch of our great science. The journal being thus cosmopolitan brings to every

chemist not only matter relating particularly to his branch of study, but also a general idea of what is going on in other fields of activity. He, therefore, who desires to keep abreast of the work of the times and avoid becoming narrow in his views and practices, can not find a better means to this end than membership in our Society. The American Chemical Society has no quarrel with any chemical sect or any institution of learning, but will endeavor to make itself useful to all. It would especially seek to foster a spirit of scientific patriotism in this country, a belief in American science and American scientists, and to diminish, to a certain extent, the blind worship of foreign institutions which, in some instances, has been so characteristic a feature of American workers. I would not say anything to discourage a young man from seeking a part of his education abroad, but I would certainly encourage foreign chemists to seek a part of their education in this country. It is not quite right for the United States to contribute so many students and so few professors. While the American student may find benefit from a course of study abroad, the foreign student would find equal benefit by a residence at some of the great institutions of learning in this country. If professors of chemistry desire to attract students from abroad they must recognize their own country in its scientific institutions. They can not afford to remain outside of the great organized body of American chemists and to send their contributions all to foreign journals if they wish their own institutions to grow in favor at home and abroad. While we are proud therefore, of our large membership, it is evident that for every one who is now a member there are at least two who should become so.

There are nearly 4000 men in the United States who are engaged directly in chemical pursuits, and it is not too much to ask that at least fifty per cent. of this number should become affiliated with the American Chemical Society. We will not consider that we have attained our normal growth if at the end of the next quinquennial period our membership shall not reach fully 2000. To this end let each of our members pledge his word and exert his influence and the work will be accomplished.

I can not close this address without expressing my thanks to

the Secretary of the Society for the efficient method in which he has conducted the work of his office, arduous and exacting as it has been, and to the Directors and Councilors of the Society for the support which they have given me in all matters connected with the executive conduct of the presidential office.

In the little which I myself have been able to do, I have had in view only one object; *viz.*, the welfare and prosperity of the Society. It may be that in some cases offence has been given to members of the Society by the manner in which my work has been done, but I am sure that those who have intimate knowledge of the motives which have actuated my conduct will bear witness to the fact that such offence was not given with malice or meaning.

To my successor I may say that he will find the officers, councilors, and directors, remaining as they do mostly unchanged, full of zeal in the work of building up the Society and ready at all times to support him in the conduct of his office.

THE DETERMINATION OF PHOSPHORIC ACID.

By H. Pemberton, Jr.

Received January 17, 1895.

THE method of determining phosphoric acid by the alkalimetric titration of the yellow precipitate, has been employed, lately, by a number of chemists and has been made a subject of investigation by the Association of Official Agricultural Chemists. A report upon the subject has been embodied in its last bulletin.

There are a few points regarding this method to which attention should be drawn.

In preparing the standard alkali its strength is, of course, established by testing it against acid of known strength. In doing this, it is important that the indicator used should be phenolphthalein, and *not* methylorange. Potassium hydroxide almost invariably contains alumina, and such a solution gives the neutral reaction with methyl orange *before* it gives it with phenolphthalein. Consequently if methyl orange is used in the standardizing and phenolphthalein is used in the titration of the

yellow precipitate, too much of the alkali will be used in the latter case, and the results will be high.

The same reasoning holds true in case a little carbon dioxide is present in the alkali.

In regard to the precipitation of the phosphoric acid by the aqueous solution of the molybdate, the following directions were given: Heat is now applied, and the solution brought to a full boil. It is then removed from the lamp, *no more heat being applied.* (This JOURNAL, **15**, 387.)

I have italicized here in order to draw attention to this point. If the volume of the phosphate solution is from fifty to seventy-five cc., it will be found, after adding five cc. of the molybdate, say three times (fifteen cc. in all) that the temperature of the solution will be about 70° C., which is about the proper temperature for the precipitation. In other words, the solution, once heated, will take care of itself, (if I may use the expression) and does not require a water-bath of definite temperature, or any testings with the thermometer.

There is another point in connection with this precipitation that is of interest. It is well known that a precipitate that has a crystalline or coarse structure is more easily washed, and is less liable to carry down impurities, than a precipitate obtained in a finely divided condition, or as a "mud." Thus in separating lime as sulphate, from iron and alumina, in Jones' process, the alcohol is not added until most of the calcium sulphate has crystallized out from the aqueous solution. Were the sulphuric acid added to the alcoholic solution the precipitate would certainly be impure. In like manner, in potassium determinations, we evaporate the solution nearly to dryness (although it takes this extra time), in order to obtain the platinum salt in a crystalline state. Again in precipitating phosphoric acid by magnesia mixture, the latter is added slowly, drop by drop, "stirring vigorously," in order to prevent contamination. In the same way, when precipitating by the aqueous molybdate, I am accustomed to run the contents of the five cc. pipette into the solution *not* in one continuous stream, but by interrupting the flow from the pipette by momentarily touching the end of the pipette with the finger, *stirring* the solution as it goes in. Thus

the precipitate does not come down *en bloc*, in presence of a great excess of molybdate, but forms in a solution that is comparatively bare of molybdenum until the precipitate is nearly all down. The washing of the precipitate is best conducted, with the use of a vacuum, on a Hirsch porcelain funnel, smallest size, or as described by Mr. B. W. Kilgore, on a porcelain disk, (the disk to be covered with filter paper) with rubber rim in three inch glass funnel. In either case, soft paper from cut filters is better than that bought in sheets. Others have used the Gooch crucible, with advantage. With the Hirsch funnel I find that a precipitate containing forty mgms. of phosphorus pentoxide is thoroughly washed by 300 cc. of water. I may say here that fifty mgms. of phosphorus pentoxide is about the largest quantity that it is well to work upon, when employing a suction-pump. Chemists who do not use suction had better employ not more than thirty to forty mgms. The phosphomolybdate is a difficult precipitate to wash, being like lead chromate in this respect.

The nitric acid, sp. gr. one and four-tenths, and the ammonium nitrate solution, are best kept in graduated glass cylinders of 200 to 300 cc. capacity, the mouths of which are kept covered by small beakers. The quantity desired to be poured out can then be read off on the graduation.

The molybdate solution (which should be neutral, and is best freed from any insoluble molybdic acid by filtration), can be kept in an ordinary narrow-mouth bottle. A wide, flat cork covers the mouth of this bottle, and through the center of this cork the stem of a five cc. volume pipette is held tight. This pipette rests, when not in use, in the molybdenum solution, and the cork prevents the entrance of dust. Mr. Kilgore has applied the ordinary nitric acid solution of the molybdate, to this volumetric process, with good results. He heats the solution on a water-bath having a constant temperature of 60° C. Mr. F. Bergami adds to his solution of the phosphate (containing already about three cc. of strong nitric acid), ten cc. of ammonia, sp. gr. 0.90, and then fifteen cc. of nitric acid, sp. gr. 1.40, and then, after heating to boiling, proceeds with the aqueous molybdate, in the usual way. Mr. L. A. Voorhees, precipitates with the nitric acid solution of the molyb-

date *in the cold*, allows to stand, at the temperature of the room, over night, and titrates in the morning. The details of these modifications are given in the 1894 report of the Association of Official Agricultural Chemists, published at Washington, D. C. Whatever modification may be used, the volumetric method will be found much quicker than the gravimetric, and, after a little experience, fully as reliable.

PHILADELPHIA, Pa.

ON THE ESTIMATION OF SULPHUR IN PYRITES.[1]

BY G. LUNGE.

Received December 20, 1894.

UNDER the above title, Mr. T. S. Gladding (This JOURNAL, June, 1894), has published several modifications of the wet assay of pyrites which call for some comment on my part, since these modifications purport to be improvements on my method, contained in the "Alkali-makers' Handbook," and extensively employed in all countries.

Some of Gladding's modifications are of a less important character, and these can be passed in review very briefly. He does not, like myself, test the sample with its natural moisture, estimating the latter in a special sample, but he dries the whole sample and weighs it out in that state. He employs a whole gram of pyrites, I only half a gram; and I do so purposely, because the washing of the precipitates is much easier, and consequently the results are more reliable with the smaller than with the larger quantity. In lieu of the mixture of acids employed by me (three volumes of nitric acid of sp. gr. 1.42 and one volume of fuming hydrochloric acid) Gladding decomposes the pyrites with a solution of bromine and nitric acid. The prescription for that solution is not correct as printed, for seventy-five grams of potassium bromide can not possibly be dissolved in fifty grams of cold water, or anything like that quantity, but this may be a clerical error, which does not matter very much, as ultimately the solution is diluted to 500 cc. I will say at once that the bromine solution works well, but no better than the acid mixture according to my prescription.

[1] Read at the Boston Meeting, December 28, 1894.

A more important modification is the following: It is well known that in the presence of iron the precipitate formed by barium chloride in a solution of sulphates can not be freed from iron, and that the results of the estimation of sulphur in this case are too low; in my publication of 1879 (*Ztschr. anal. Chem.*, **19**, 419) I found on the average 0.19 per cent. too little sulphur, unless the iron had been previously removed from the solution. Fresenius has also worked on this subject, and Jannasch and Richards, in 1889, completely elucidated it by proving that a double sulphate of barium and iron was formed in this case. Gladding gives a similar explanation, without mentioning the more complete investigations of his predecessors, which would have saved him the trouble of working out the matter for himself. I had already long ago dealt with that difficulty by proposing, in 1889, that method which was afterwards embodied in the "Alkali-makers' Handbook," *viz.*, precipitating the iron by ammonia, washing the ferric hydroxide, and precipitating the sulphate in the filtrate by barium chloride. Gladding asserts, however, that "the most careful washing failed to wash out all the sulphur from the ferric hydroxide," and he therefore proposes to wash the hydroxide as well as possible and to dissolve it afterwards in diluted hydrochloric acid, thereupon treating that solution with barium chloride; evidently with the tacit assumption that the small quantity of sulphide present in that solution is accurately enough estimated as barium sulphate, in spite of the large quantity of iron present; but that assumption is far from self-evident, nor does it actually represent the truth, as we shall see.

It is quite evident that Gladding, although he knows and quotes the "Alkali-makers' Handbook," and although he entirely adopts the prescription given there (page 93) for the *precipitation* of the ferric hydroxide, which deviates not unessentially from those previously given by Fresenius and others, has not completely followed the instructions for the *washing* of the precipitate given immediately after in the following words: "Filter hot, and wash on the filter with hot water, avoiding channels in the mass, but so that the whole precipitate is thoroughly *churned up* with the water each time." Many hundreds of pyrites tests made in my own and other laboratories have

proved that by following the above instructions the washing of the ferric hydroxide is accomplished in from half an hour to an hour, that the number of washings need not exceed five, and the bulk of the liquid, apart from the original filtrate, need not exceed 100 to 150 cc., and *that no trace of sulphur is left in the ferric hydroxide*, as evidenced by drying the precipitate, fluxing it with pure soda, dissolving it in water, and testing the solution for sulphate. It is true that the students in my laboratory have sometimes failed to get out all the sulphur, but in *every* case through having washed in the usual way, instead of that described above; and the same men have succeeded in *every* case, after their attention had been drawn to this point.

There is another difference between Gladding's and my own manner of proceeding. I prescribe heating the solution of the sulphate to the boiling-point, as well as that of the barium chloride, adding the latter to the former all at once, allowing to stand for half an hour only, and then at once filtering and washing while the liquid is quite hot. I had convinced myself that under these circumstances the precipitate filters most easily, and no barium sulphate whatever subsequently separates from the filtrate. Gladding, however, not merely adheres to the old and useless prescription of letting the liquid stand over night after the precipitation, but he adds to this a novel and most tedious way of effecting the precipitation, *viz.*, adding fifty cc. of barium chloride solution quite slowly, one drop per minute. This will take about an hour, instead of a few seconds, as in my method.

I considered it my duty to find out whether the method recommended by Gladding is better than mine, or inferior to it, or equivalent with it; and in the last case, which of the two is easier and quicker to execute. For this purpose a sample of Spanish pyrites was selected which was triturated as usual and mixed in the most careful manner. The tests were made by one of my demonstrators, H. von Keler, under my constant personal supervision. First of all the sample was tested exactly according to the method laid down in the "Handbook," with the following results: 50.17; 50.42; 50.20; 50.23; 50.19; average, 50.24 per cent. The insoluble amounted to 1.42 per cent; the moisture to 0.47 per cent. I abstain from reducing the percentages to the dry state, as being unnecessary in this case.

As the next step, a number of samples were decomposed by Gladding's mixture of bromine solution and nitric acid. We found his prescription in this item to be perfectly correct; it is not feasible to hasten the process (which is much lengthier than that used by myself), for instance, by filling the water-bath from the first with hot water. Any attempt to do such a thing ends in an over-violent reaction, and a loss by spurting and separation of free sulphur. We tested, of course, our bromine and potassium bromide, and found them quite free from sulphuric acid.

Three of the samples thus decomposed, according to Gladding, were precipitated exactly according to his method (one hour's precipitation, twelve hours' settling), another three samples according to mine (precipitating all at once and filtering after half an hour). The results were:

Gladding's Method.	Lunge's Method.
50.24	50.24
50.24	50.22
50.30	50.28
50.26	50.25

We see that both methods of precipitation give identical results, and these also entirely agree with the tests made from the first according to the "Handbook" method, *viz.*, 50.24. The conclusions to be drawn therefrom are: 1. Since both methods of precipitation yield the same result, my expeditious method of precipitation and filtration, which, inclusive of washing, takes about an hour, is preferable to Gladding's method, requiring about twelve hours. 2. Since Gladding's bromine method for decomposing pyrites yields results identical with that prescribed by myself, there is no reason for abandoning the latter and adopting a more tedious method, unnecessarily employing such a disagreeable reagent as bromine.

I understand from a private communication of Mr. Gladding's that he attributes the greatest value to his manner of precipitating the barium sulphate, and that in his opinion by operating in my way barium chloride is always carried down with the sulphate, making the results too high by 0.20 to 0.40 per cent. It would have been most remarkable if that point had been over-

looked in the many thousands of tests made according to my methods by perhaps a hundred different chemists; but in order not to incur any reproach, I had this point put to another searching investigation. Mr. W. Jackson made five most careful tests of another sample of pyrites, decomposing and otherwise treating them absolutely in the same way, but making the precipitation in two cases by Gladding's, and in three cases by my method. The results were:

Lunge's Method.	Gladding's Method.
50.59 per cent.	50.60 per cent.
50.63 " "	50.66 " "
50.56 " "	....
Average, 50.59 " "	Average, 50.63 " "

This affords another thorough refutation of Gladding's assertion.

In all analyses made up to this point the ferric hydroxide had been precipitated and washed five times, exactly in the way described by me; in every case it had been afterwards tested by fluxing with soda, but no trace of sulphur had ever been found. This furnished an additional (although unnecessary) proof that Gladding's assertion in that respect is equally unfounded, and that the treatment described by him (dissolving the ferric hydroxide in hydrochloric acid and precipitating by barium chloride) is quite useless, when observing the precautions in washing, pointed out by me. Still I thought it advisable to find out how Gladding's process would work in cases where, by some mistake, a little sulphur had been left in the hydroxide, and I grant that in important cases the latter ought to be tested in some way or another for any sulphur left behind. I further grant at once that in this case Gladding's method, as described, is more expeditious than mine: drying the ferric hydroxide, detaching it from the paper, mixing it with pure sodium carbonate, fluxing it in a platinum crucible (in such manner that no sulphur from the gas can get into the mass, *e. g.*, in a hole made in asbestos cardboard), dissolving in water and precipitating the sulphur by barium chloride. It is hardly necessary to say that I did not choose this plan without first considering the very simple method described by Mr. Gladding; but I rejected

it, since Fresenius had proved that barium sulphate is very distinctly soluble in an acid solution of ferric chloride. But as Gladding now asserts that the direct solution of the ferric hydroxide in hydrochloric acid yields accurate results, it became incumbent upon me to examine this statement.

Eight samples of our pyrites were decomposed, and the ferric hydroxide was precipitated under absolutely equal conditions of dilution, temperature, and quantities of reagents. The washing was purposely not continued as far as it ought to have been; and as some previous experiments had shown that no uniform degree of exhaustion can be attained by incomplete washing, we estimated in all cases the *total* sulphur, separating, of course, that which was found in the filtrate and that which was left with the ferric hydroxide. Four of the eight samples were treated by Gladding's prescription, and four by my own system. The results were:

Lunge (fluxing with sodium carbonate).			Gladding (dissolving in hydrochloric acid)		
Filtrate.	Precipitate.	Total.	Filtrate.	Precipitate.	Total.
49.64	0.60	50.24	48.98	1.03	50.01
49.36	1.01	50.37	48.84	1.39	50.23
49.07	1.21	50.28	49.02	1.07	50.19
49.25	1.04	50.29	49.30	0.73	50.03
Average,		50.29	Average,		50.09

This proves that Gladding's method does not, in this particular, give accurate, but *low* results (by 0.20 per cent.); with less complete washing the discrepancy would evidently have been even greater. The total sulphur found by my process, on the other hand, agrees quite satisfactorily with the correct analyses quoted before.

The final conclusion of this investigation must be: That in most points Gladding's method is correct, but in *not a single case* more so than my method; his modifications can not be approved, as they greatly lengthen the time required for the analysis, without any corresponding advantage whatever. In one point which forms the principal novelty in Gladding's process, he is decidedly *wrong*. It is not true that it is unavoidable to leave any sulphur in the ferric hydroxide; on the contrary this is very easy to avoid. If it has, after all, happened by incorrect manip-

ulation, Gladding's plan will *not* get out all the sulphur, but my plan (fluxing with soda) must be adopted.

I have shown that there is not a single point recommended by Gladding, in deviation from my method, which is fit for adoption, and I must conscientiously advise my brother chemists to adhere to the method just as I have laid it down in the "Alkali-makers' Handbook."

In conclusion I would add that I have also tried the method recommended by F. Johnson (*Chem. News*, *1894*, **70**, 212), omitting to precipitate the iron, but reducing it by sodium hypophosphite to the state of protochloride. Even when working precisely as described by the author, the results were so widely off the truth, that I can make nothing whatever of this plan.

IMPROVEMENT IN THE MANUFACTURE OF ACETONE.[1]

By E. R. Squibb, M.D.

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THE increasing use of acetone as a chemical solvent, and especially the relation of acetone to the manufacture of chloroform, gives importance to any improvement in its production.

Up to this time the writer knows of no process of manufacture except by the destructive distillation of acetates at high temperature. The acetates are charged into stills and heated as long as they yield any acetone. Then the acetates being decomposed to waste carbonates are discharged and the stills recharged with fresh acetate, making an interrupted process of repeated charging and discharging and heating and cooling. This process is very old; but two patents have been taken out in this country on some details of the process and apparatus.

The writer proposed to himself to make acetone directly from acetic acid by a continuous process, and has accomplished that object.

In Gmelin's Handbook of Chemistry, Cavendish Society edition, *1853*, **8**, 291, under the head of decomposition of acetic acid by heat, much work is given where the vapor of acetic acid was

[1] Read before the N. Y. Section, January 11, 1895.

passed through heated tubes, acetone being one of the products; and, on this line of investigation, the writer's work was taken up.

It was not difficult to see that the discrepant results reached by the authorities were due to differing physical conditions, and different degrees of heating, since it was mechanically quite certain that a current of vapor passing through a stationary tube, heated from below, whether empty or filled, could not be heated to the same degree in all parts of the tube, and therefore could not give the same decomposition in all parts.

The work undertaken was commenced in very long-necked glass bulbs, held in a horizontal position, so that they might be stationary or be revolved by hand, and these were heated by a bath of Wood's metal—the acid being passed in, and the products coming out through horizontal tubes in the long necks.

Experiences with these bulbs led to much better mechanical devices. A small flask was arranged as a still, and from this, by a gas-burner, a constant current of acetic acid vapor could be produced at any desired rate. The rate was regulated by the rate of supply of liquid acid from an elevated graduated supply vessel, the supply going to the still through a glass tube, in which the rate of dropping was seen and controlled by a stop-cock. Then, by varying the acid supply and the heat from the burner, the boiling liquid in the still could be kept at about a constant level, and with a controllable known rate of vapor supply.

At some distance from this end of this apparatus the condensing apparatus was arranged to receive the distillates. The products of distillation were first received in a flask where most of the watery vapor and undecomposed acid was condensed, but where the temperature continued so high that but a mere trace of acetone was arrested there. From the neck of this flask the remaining gases and vapors passed through a good condenser, which delivered the remainder of the water and undecomposed acid and the acetone into a flask immersed in an ice-bath. Here almost all the condensible vapors were condensed. The gases and uncondensed vapors were taken from the neck of this flask to a small wash-bottle supplied with water, by which the current of gases was washed. Here waste acetone enough was caught to increase the volume of contents to a point at which all went off

together in the current of gases, and the level remained constant. Next was a wash-bottle containing a strong solution of sodium hydroxide. Through this the residual gases were passed in order that most of the carbon dioxide might be combined. Finally, the gases were passed through another small wash-bottle containing water. At the small exit tube of this bottle the gases were tested for inflammability, and the proportion of methane and carbon monoxide was estimated by the absence or the degree of inflammability. Except at the times of testing, this exit tube was connected to a Sprengel water-pump, and a minus pressure of one to six cm. of mercury was maintained on the entire apparatus. This served to relieve all joints and connections and caused all the leakages to be inward, whilst a mercury-gauge at each end gave due notice of obstruction or irregularities.

These two ends of the apparatus remaining constant, the intervening space was occupied by the varying form of distilling or decomposing apparatus. An earthenware drain-pipe, with movable tile ends served as a furnace. This drain-pipe, supported in a horizontal position, had six holes drilled above and below. Each lower hole was large enough to admit a Bunsen burner with limited air space around it, while the holes on top, to give exit to the products of the combustion were smaller. The decomposing tubes or stills of wrought iron, with cast iron ends, occupied this drain-pipe furnace, being connected with the vapor supply apparatus at one end and the condenser at the other.

Much preliminary work was necessary in getting the apparatus in good working order, and in following up tangential points, but these are passed over, and only the important work given—and that not always in the order in which it was done, but in an order which brings the results into a more logical sequence more easily understood.

Two strengths of acetic acid were used. First, an acid containing thirty-six per cent. of absolute acid. But as this gave distillates unnecessarily dilute it was generally given up in favor of a sixty per cent. acid, although the reactions were not noticeably different in the use of the two strengths. Hence with two exceptions the results given are from a sixty per cent. acetic acid.

Reducing the work from the disorderly way in which it was done to a natural order, and rejecting what was not trustworthy, it is best to begin with some repetitions of work already long on record. (See Gmelin's Handbook, and other authorities.)

A tube of wrought iron about thirty-six cm. (fourteen inches) in length by six and five-tenths cm. (two and five-tenths inches) internal diameter, reduced at each end to tubing of about six-tenths cm. (one-fourth inch), was held stationary in the center of the furnace, and connected at one end with the acid vapor supply and at the other with the condensers. This tube could be heated by the gas-burners to any desired degree up to a dull red heat. The trials were made under as nearly the same conditions as practicable, the running time being about three and five-tenths hours, and under close observation. The amount of sixty per cent. acetic acid which could be passed in, in vapor during this time, varied much—generally 250 to 350 cc. The quantities used were always reduced to absolute acid ($HC_2H_3O_2 = 59.86$), and the results are given in the same acid, but a high degree of accuracy was impracticable, and therefore not aimed at.

(1) With the tube empty and heated nearly to redness at first, and finally to a dull red heat, 290 cc. of sixty per cent. acid = 174 grams absolute acid, was passed in in three and five-tenths hours. About 111 grams of this acid passed through unchanged, and sixty-three grams were decomposed. That is, about 63.8 per cent. came through unchanged, and 36.2 per cent. were decomposed. In the first receiving flask, kept hot by the vapor, there was no acetone, but only 132 cc. of a fifty-three per cent. acid. In the second flask, in the ice-bath, there was 115 cc. of a thirty-six per cent. acid; and this liquid, roughly estimated by the iodoform test, contained ten to twelve per cent. of acetone. From the final wash-bottle came a stream of inflammable gas—probably methane and carbon monoxide—that would burn almost continuously.

(2) Next, this stationary tube was filled with coarsely granulated pumice-stone, freed from large pieces and from dust, and so tightly packed as to have spring enough to keep the tube full when expanded by heating. Into this, in three and five-tenths

hours, 189 grams of absolute acid, in vapor, were passed, and yielded in the first, hot flask 103 cc. of fifty-four per cent. acid = 55.62 grams absolute acid. In the second, ice-bath flask 138 cc. of 38.4 per cent. acid = 52.97 grams of absolute acid, making 108.6 grams out of 189 grams distilled over unchanged, and 80.4 grams decomposed. The contents of this second flask were about 14.5 per cent. acetone. The stream of inflammable gases was estimated as being not less but rather greater than with the empty tube.

(3) Next, took the pumice from the tube, divided it into two parts, and rejecting one-half, intimately mixed with the other half 500 grams of dry, precipitated barium carbonate. Charged the tube with this mixture, having a little unmixed pumice at both ends. Barium carbonate was selected to multiply surface, as being a rather heavy powder that would not shrink nor fuse, nor be likely to decompose.

About 450 cc. of sixty per cent. acid = 270 grams of absolute acid were passed, in vapor, in three and five-tenths hours, into this mixture, heated as before. The distillate in the first, hot flask was eighty-one cc. of acid water of only one and six-tenths per cent. = one and three-tenths grams absolute acid. In the second ice-bath flask was 227 cc. sp. gr. about 0.955, containing one and two-tenths per cent. acid = two and seven-tenths grams absolute acid. Of the 270 grams passed in, four grams only distilled over unchanged, while 266 grams were decomposed. The 227 cc. of distillate in the second flask contained about 23.3 per cent. of acetone. This proportion gives about twenty per cent. of acetone from the 266 grams of absolute acid used. The stream of inflammable gases was very much greater than in the other experiments, burning with an almost continuous large flame.

The desired splitting of acetic acid to yield acetone requires two molecules of the acid to yield one molecule of acetone, the residuary products being one molecule each of carbon dioxide and water. That is, 120 grams of absolute acetic acid should give

58 grams of acetone,
44 " " carbon dioxide,
18 " " water, or

by percentage the acid should give

48.33 per cent. acetone,
36.67 " carbon dioxide,
15.00 " water.

When marsh-gas or methane (CH_4) and carbon monoxide (CO) are formed it is probably largely, if not entirely, through a secondary decomposition of the acetone by a higher heat than that which gives the primary decomposition into acetone, carbon dioxide, and water, and when acetone and methane are produced together, it is rational to suppose that inequalities of heating are the cause. That is, if acetone be produced it indicates that the exact conditions required are present at that time and place. Then it follows that if these exact conditions be extended throughout the whole time and place of reaction the acetone splitting of the acid only can occur, and no methane or other products of other reactions can be produced. The conditions for producing these different reactions are doubtless different degrees of heating, and uniformity of reaction can be expected only from uniformity of heating. And the differences in the degrees of heat required to produce the different reactions here, do not seem to be great.

The physical and mechanical conditions of heating a stationary tube can not possibly yield an equal degree of heating to the contents of such a tube, especially where only a part of such contents is in motion. Even if the whole outside of the tube could be equally heated—as it could not be practically—the contents would be cooler from circumference to center. But in this case, where a current of vapor at about 100° C. is passed continually, into a tube the outside of which is kept unequally heated to 500° or 600° C., and where this current has to find its way at varying speed through varying friction and expansion, only a varying decomposition can be possible, and the conclusion must be that if uniform decomposition is to be reached it must be through uniform conditions.

Equable heating in a stationary tube, under the conditions of this process, being impracticable, it became necessary to devise some better form of still; and a careful consideration of the principles involved, and the especial mechanical difficulties of this

decomposition, led the writer to a form of rotary still, which, after some alterations and modifications, has proved successful.

A wrought-iron tube about thirty-six cm. (fourteen inches) long by 12.7 cm. (five inches) in diameter, contracted at the ends to central hollow journals of about two cm. (three-fourths inch) external diameter and one and two-tenths cm. (five-tenths inch) bore, free to revolve, was supported in the center of the eighteen cm. (seven inches) drain-pipe furnace and connected at one end with the vapor supply and the other with the condensers by air-tight glands or "stuffing-boxes." The ends were provided with charging and discharging openings which could be closed air-tight, and the still was revolved slowly by means of a pulley on one end of the hollow shaft. A small stationary tube passed into the still through the revolving shaft to convey the acid vapor to the entrance of the still at one end, and a similar tube gave exit to the products of the decomposition at the other, condenser end. It was necessary to protect this tube from obstruction by dust carried by the current of vapors, and this was done by a cartridge of rolled up, wire cloth, filled with glass wool. This rotary still was driven at the rate of three to six revolutions per minute by a small water-motor, and was found to heat with great equability as it revolved over the burners. Inside of the still, at equal distances apart on the periphery, five L-shaped, longitudinal strips of sheet iron were riveted. These were necessary to prevent the charge from sliding round as the iron became smooth, and they were found to carry the charge round, turn it over, and mix it most effectively at each revolution. Thus, while by the revolutions over the source of heating the shell was heated very uniformly, this continuous moving and turning over of the contents must bring all parts of the charge, solids and vapors alke, in successive contact with the hot surfaces and the cooler atmosphere of the still, and thus secure a fair degree of equable heating. The still being about one-third filled with the solid charge and slowly rotated, the charge occupies principally,—not the bottom of the still directly over the fire, but the ascending third which has just been over the fire. Then, as the charge is carried up, the superficial cooler portion, too deep to be held by the longitudinal shelves, slides back upon the hot surface below,

while the portion carried on by the shelves falls back, shelf by shelf, from contact with the hot shell through the atmosphere of vapor, upon the cooler portions below to be mixed and carried up again in a similar order. At the same time the whole atmosphere of the still is filled with dust which becomes very fine, and very largely multiplies the surfaces of contact with the vapor, for decomposition, whilst the vapors pass slowly and uniformly and with a minimum of friction to the exit at the condenser end. If the motion and heating of a charge in this still be compared with those in a stationary still with a horizontal stirrer driven by a vertical shaft, the advantages of the former will be easily understood. The latter moves the charge round over the fire, but has a comparatively slight effect in bringing new portions of the charge successively in contact with the heating surfaces, and it does not tend to prevent horizontal stratification of the charge with consequent irregular heating; and it does not tend to the fullest contact of the vapors with the surfaces of the charge, where the decomposition probably takes place. After the inevitable number of trials and adjustments and breakings down, the following successful experiments are selected from a large number.

(4) As a parallel experiment to (1) with the stationary still, the rotary still was used empty.

About 200 cc. of thirty-six per cent. acid = seventy-two grams of absolute acid was slowly passed into the heated, rotating, empty still.

The first hot flask of distillate contained thirty-three cc. of acid of 14.6 per cent. = 4.82 grams absolute acid.

The second ice-bath flask contained 142 cc. of acid acetone 12.6 per cent. = 17.89 grams absolute acid. Then $4.82 + 17.89 = 22.71$ grams absolute acid distilled over unchanged. Then seventy-two grams $- 22.71 = 49.29$ grams of acid decomposed. The second distillate gave an estimate of 12.1 grams acetone. Then as 49.29 acid : 12.1 acetone :: 100 : 24.5 per cent. acetone from the acid. The current of inflammable gas was considerable, but less than in (1).

(5) The rotary still was charged with about a liter of the same granulated pumice used in (2), and when heated about 295 cc.

of sixty per cent. acid = 177 grams of absolute acid was passed in, in vapor during three and five-tenths hours.

The first distillate, hot flask, had 108 cc. of acid water of four and four-tenths per cent. = 4.75 grams acid.

The second distillate, ice-bath flask, had 116 cc. acid acetone two and four-tenths per cent. acid = 2.78 grams acid.

Then 4.75 + 2.78 = 7.53 grams acid came over unchanged, out of 177 grams passed in; or, 177 — 7.53 = 169.47 grams decomposed.

The acetone estimated by iodoform was 24.3 per cent. of the acid decomposed.

(6) About 500 grams of precipitated barium carbonate was put into the rotary still on top of the charge of pumice, and when the whole was heated, 380 cc. sixty per cent. acid = 288 grams of absolute acid was passed in, in vapor during three and five-tenths hours.

The first distillate was 108 cc. of acid water containing three and nine-tenths grams acid.

The second distillate was 135 cc. of acid acetone containing two and seven-tenths grams acid.

228 grams acid — six and six-tenths grams over unchanged = 221.4 grams decomposed.

The estimated acetone was sixteen per cent. of the acid decomposed.

Much inflammable gas throughout the process.

(7) About 456 grams of precipitated barium carbonate put into the cleaned-out rotary still, and when heated 510 cc. of thirty-six per cent. acid = 183.6 grams absolute acid was passed in, in four and five-tenths hours. About 24.5 grams of acid came over unchanged, leaving 159.1 grams, decomposed.

The acetone was estimated at 53.7 grams, or about thirty-four per cent. of the decomposed acid.

(8) Charged the rotary still with 1000 grams of dry barium acetate and distilled this acetate as long as it would yield a distillate, and until it was reduced to 770 grams of barium carbonate quite free from acetate. This yielded acetone estimated by iodoform at about sixty per cent of the theoretical quantity.

When the distillation from the acetate had ceased the receivers were changed and 490 cc. of sixty per cent. acid = 294 grams

of absolute acid were passed into this charge of carbonate in about four and five-tenths hours.

The distillate was received in five fractions.

1st.	37	cc.	of	acid	water	containing	15.6	per	cent.	acid	or	5.77	grams.
2nd.	256	"	"	dilute	acetone	"	4.4	"	"	"	"	11.26	"
3rd.	230	"	"	"	"	"	9.6	"	"	"	"	22.08	"
4th.	46	"	"	"	"	"	11.0	"	"	"	"	5.06	"
5th.	26	"	"	"	"	"	17.6	"	"	"	"	4.58	"
	595	cc.										Distilled over undecomposed, 48.75	grams.

294 grams — forty-nine grams = 245 grams decomposed.

In each of the second and third flasks was about forty cc. of water at the start. Then eighty from 595 gave 515 cc. of total distillate from the 490 cc. fed in.

Acetate required from 245 grams acid 118 grams. Estimated yield seventy-one gram or sixty per cent. of the required yield.

On the following day, without having opened the still, it was reheated and 530 cc. of sixty per cent. acid = 318 grams of absolute acid was passed in, in vapor. From low street pressure in the gas-mains the heat on this day was deficient.

1st distillate	50	cc.	acid	water	containing	19.6	per	cent.	acid	or	9.8	grams.
2d "	255	"	dilute	acetone	"	10.0	"	"	"	"	25.5	"
3d "	138	"	"	"	"	6.0	"	"	"	"	8.3	"
	443	cc.									43.6	grams.

318 grams — forty-four grams = 274 grams acid decomposed.

Acetone required from 274 grams acid 132 grams. Estimated yield ninety-five grams or seventy-two per cent. of the required yield.

On the day following, again without opening the still, in about four hours, passed in 535 cc. of sixty per cent. acid = 321 grams of absolute acid.

1st dis., hot flask,	22	cc.	acid	water	containing	7.6	per	cent.	acid	or	1.67	gms.
2d " ice-bath,	258	"	dilute	acetone	"	4.8	"	"	"	"	12.38	"
3d " "	131	"	"	"	"	7.6	"	"	"	"	9.96	"
	411	cc.									24.01	gms.

321 grams — twenty-four grams = 297 grams acid decomposed.

Acetone required by theory from 296 grams acid 143 grams. Obtained by estimate about 113 grams or nearly eighty per cent. of the required yield.

Now, upon cooling and opening the still, samples taken from various parts of the contents were all found to be barium carbonate and free from acetic acid.

During the progress of these distillations from pumice stone, from carbonates, and from the empty stills alike, whenever the supply of acid vapor was cut off the distillation almost instantly ceased, showing that there was then nothing in the still to decompose.

This, then, is the improved, continuous process for the production of acetone directly from acetic acid, which avoids and saves the intermediate steps of forming and decomposing acetates.

The formation of acetates in the still was repeatedly tried with both barium and calcium carbonates, but always failed until the temperature was reduced to about the boiling-point of water, or the condensing-point of watery vapor, and then the acetates formed, cohered and adhered to the ribs and shell of the still, and no longer moved until again decomposed by a higher heat.

Corresponding trials were made with calcium carbonate and with calcium acetate decomposed to carbonate, with results very similar to those above given, but the barium carbonate seemed to answer best, possibly because it yields a heavier powder that occupies less space and moves better.

When commercial calcium acetate was used, tarry matters obstructed the exit tubes and contaminated the distillates. The portion of these tarry matters that was reduced to charcoal in the still, and there mixed with the carbonate, seemed to be rather beneficial than obstructive. But on the whole the process appeared to do better with carbonates reduced from acetates that were made for the purpose from good materials. As the process seems to be rather a mechanical or physical one of surface contact, it would be reasonable to expect better results from reduced carbonates than from precipitated carbonates. And it is still an open question whether, on the large manufacturing

scale, with better control of the essentials, heat and motion, pumice or bone black, or some other such substance, will not be better than the carbonates. Of one thing the writer is quite convinced, and that is that the close regulation of the heating within narrow limits of variation, is far the most important element in the process. Within very narrow limits, too little heat gives undecomposed acid, while too much gives inflammable gases in place of acetone. But on the large scale this element will be under much better control, whilst a proportionately longer still will give the acid vapor farther to go and a prolonged exposure to the limited heating and contact.

There are no patents sought for on this process or apparatus.

The dilute acetone from this process is fairly good and clean, and is colorless except for the action of the free acid contained on the iron tubing. With the free acid the specific gravity by hydrometer varies between 0.93 and 0.97. No part of the distillate has more than a thin film of oil on the surface too small to be measured, and this oily surface is only in the first flask with the acid water. On further dilution of the ice-bath distillate it is rendered opalescent for a minute or two and then becomes again transparent.

This distillate (undiluted) is a good solvent for many substances, and is probably pure enough for the manufacture of chloroform.

When allowed to stand some days upon caustic lime and then poured off and rectified, it is much improved in character and strength, and is then adapted to a still larger number of uses, and is perhaps better adapted to the manufacture of chloroform.

The product of this first rectification was then digested with about ten per cent. of dry calcium chloride. This abstracted most of the water and settled in dense solution at the bottom of the bright yellowish acetone. This latter was separated and distilled, and again digested for several days with ten per cent. of fresh calcium chloride, being frequently well shaken. Again twice separated and distilled from fresh portions of calcium chloride, in a capacious flask with a good Hempel tube filled with small glass marbles, and the whole apparatus filled with well-dried air, and distilled directly into specific gravity bottles, such as are described in the *Ephemeris*, **4**, 1448—it gave six

fractions, four of which had the specific gravities at $\frac{15}{15}$° C., as follows: First, 0.79662; second, 0.79704; third, 0.79712; sixth, 0.79793. The irregularities of these differences are doubtless due to differences in rate of boiling, yet they demonstrate conclusively that the first fraction can not be anhydrous.

Authorities differ much as to the specific gravity of acetone. The lowest noticed is, given by W. H. Perkin, Ph.D., F. R. S., in the *J. Chem. Soc.*, 1884, **45**, 478. He gives the specific gravity at $\frac{15}{15}$° as 0.79652, and at $\frac{25}{25}$° as 0.78669—and says this is lower than that usually observed, but agrees pretty closely with that of Linnemann, who obtained $\frac{15}{15}$° = 0.7975. Thorpe's number, calculated for this temperature, gave $\frac{15}{15}$° = 0.80244. Judging from the circumstance that the writer's fractions did not agree, and that therefore there was no constant boiling-point to his distillate, and hence no part anhydrous—his and Perkin's results are both too high.

Notwithstanding this, the writer accepts, for the present at least, his own result as a basis for the following specific gravities of dilutions. His best results as obtained by the use of his above-mentioned specific gravity bottles, and a sensitive thermometer in tenths of a degree, recently compared with a standard, are as follows:

At $\frac{4}{4}$° C. 0.808157. At $\frac{15}{15}$° C. 0.796620. At $\frac{25}{25}$° C. 0.786988.

It was first desirable to know whether dilutions of acetone with water were mere mixtures, or whether as in the case of alcohol there was molecular combination with contraction and elevation of temperature. It was found that when forty cc. of acetone of about ninety per cent. was mixed with forty cc. of water there was a contraction of three and two-tenths cc., and an increase of temperature of 5.6° C., with an effervescence of gas as in alcohol.

The proportion of ten grams of recently boiled distilled water added to ninety grams of this distillate, mixed by connecting two flasks with the weighed quantities, and passing the liquids back and forth without exposure to external air or loss of vapor, gave the following specific gravities:

Acetone at $\frac{4}{4}$° C. 0.8371. $\frac{15}{15}$° C. 0.8260. $\frac{25}{25}$° C. 0.8168 for ten per cent. of water, or ninety per cent. acetone.

This method of dilution by weighing the acetone and water separately in flasks and then connecting the flasks for mixing without loss of vapor or outer air contact was adopted for the basis of the following Acetone Table. The lines of the table that are given in heavy-faced type are given from actual observation, and the remainder by interpolation.

Acetone = C_3H_6O, or dimethyl ketone = CH_3COCH_3 is a transparent, colorless, mobile, light, inflammable liquid of an agreeable spirituous or ethereal odor, with a suggestion of mint, and a sharp, biting taste. The suggestion of mint in the odor varies in strength in different samples, and probably does not belong to acetone, but comes from a minute trace of impurity. It boils at 56.3° C. (Regnault). The specific gravity when very nearly anhydrous is at $\frac{4^\circ}{4^\circ}$ C. 0.808157, at $\frac{15^\circ}{15^\circ}$ C. 0.796620, at $\frac{25^\circ}{25^\circ}$ C. 0.786988. It mixes in all proportions with alcohol and water, and is a very general solvent, dissolving many substances that are insoluble in alcohol.

ACETONE TABLE.

The lines of figures in broad-faced type are given from actual observation. The remainder of the table is interpolated.

The Acetone assumed for the basis of the table was not absolutely anhydrous, though probably very nearly so.

In the percentages no account is taken of the weight of the gases liberated on mixing acetone with water.

Specific Gravity at			Percentage by weight.	Specific Gravity at			Percentage by weight.
$\frac{4^\circ}{4^\circ}$ C.	$\frac{15^\circ}{15^\circ}$ C.	$\frac{25^\circ}{25^\circ}$ C.		$\frac{4^\circ}{4^\circ}$ C.	$\frac{15^\circ}{15^\circ}$ C.	$\frac{25^\circ}{25^\circ}$ C.	
0.8082	**0.7966**	**0.7870**	**100**	0.8524	0.8425	0.8338	84
0.8111	0.7995	0.7900	99	0.8549	0.8453	0.8366	83
0.8139	0.8025	0.7930	98	0.8575	0.8481	0.8394	82
0.8168	0.8054	0.7959	97	0.8600	0.8508	0.8422	81
0.8197	0.8084	0.7989	96	**0.8626**	**0.8536**	**0.8450**	**80**
0.8226	0.8113	0.8019	95	0.8651	0.8561	0.8476	79
0.8255	0.8142	0.8049	94	0.8676	0.8587	0.8502	78
0.8284	0.8172	0.8079	93	0.8701	0.8612	0.8528	77
0.8313	0.8201	0.8109	92	0.8726	0.8637	0.8554	76
0.8342	0.8231	0.8138	91	0.8752	0.8663	0.8580	75
0.8371	**0.8260**	**0.8168**	**90**	0.8777	0.8688	0.8605	74
0.8397	0.8288	0.8196	89	0.8802	0.8714	0.8631	73
0.8422	0.8315	0.8225	88	0.8827	0.8739	0.8657	72
0.8448	0.8343	0.8253	87	0.8852	0.8764	0.8683	71
0.8473	0.8370	0.8281	86	**0.8877**	**0.8790**	**0.8709**	**70**
0.8498	0.8398	0.8309	85	0.8900	0.8813	0.8732	69

Specific Gravity at $\frac{4°}{4°}$ C.	Specific Gravity at $\frac{15°}{15°}$ C.	Specific Gravity at $\frac{25°}{25°}$ C.	Percentage by weight.	Specific Gravity at $\frac{4°}{4°}$ C.	Specific Gravity at $\frac{15°}{15°}$ C.	Specific Gravity at $\frac{25°}{25°}$ C.	Percentage by weight.
0.8923	0.8836	0.8756	68	0.9469	0.9392	0.9332	43
0.8946	0.8858	0.8779	67	0.9489	0.9412	0.9353	42
0.8969	0.8881	0.8803	66	0.9508	0.9433	0.9375	41
0.8992	0.8904	0.8826	65	**0.9527**	**0.9454**	**0.9397**	**40**
0.9014	0.8927	0.8850	64	0.9541	0.9469	0.9413	39
0.9037	0.8950	0.8874	63	0.9554	0.9484	0.9430	38
0.9060	0.8973	0.8897	62	0.9567	0.9499	0.9446	37
0.9083	0.8996	0.8921	61	0.9580	0.9514	0.9462	36
0.9106	0.9019	0.8944	60	0.9594	0.9529	0.9479	35
0.9129	0.9041	0.8968	59	0.9607	0.9544	0.9495	34
0.9151	0.9064	0.8991	58	0.9620	0.9559	0.9512	33
0.9174	0.9087	0.9015	57	0.9634	0.9574	0.9528	32
0.9197	0.9110	0.9038	56	0.9647	0.9589	0.9545	31
0.9220	0.9133	0.9062	55	0.9660	0.9604	0.9561	30
0.9243	0.9156	0.9086	54	0.9674	0.9619	0.9578	29
0.9266	0.9179	0.9109	53	0.9687	0.9635	0.9594	28
0.9289	0.9202	0.9133	52	0.9700	0.9650	0.9611	27
0.9311	0.9224	0.9156	51	0.9714	0.9665	0.9627	26
0.9334	**0.9247**	**0.9180**	**50**	0.9727	0.9680	0.9644	25
0.9354	0.9268	0.9202	49	0.9740	0.9795	0.9660	24
0.9373	0.9289	0.9223	48	0.9754	0.9710	0.9677	23
0.9392	0.9309	0.9245	47	0.9767	0.9725	0.9693	22
0.9411	0.9330	0.9267	46	0.9780	0.9740	0.9709	21
0.9431	0.9351	0.9288	45	**0.9794**	**0.9755**	**0.9726**	**20**
0.9450	0.9371	0.9310	44				

REPORT OF COMMITTEE ON ATOMIC WEIGHTS, PUBLISHED DURING 1894.[1]

By F. W. Clarke.

Received January 2, 1895.

To the Members of the American Chemical Society:

YOUR committee upon atomic weights respectfully submits the following report, which summarizes the work done in this department of chemistry during 1894. Although the volume of completed determinations is not large, it is known that several important investigations are in progress, from which valuable results may be expected in the near future. It is in this country that the greatest activity exists, and that the greatest progress is being made at present; and the preparation of these reports is therefore a peculiarly appropriate function of the Society. The data for 1894 are as follows:

The H:O ratio.—An interesting attempt at the indirect measurement of this ratio, which is the base line upon which our sys-

[1] Read at the Boston Meeting, December 28, 1894.

tem of atomic weights depends, has been made by Julius Thomsen.[1] His determinations are really determinations of the ratio $NH_3 : HCl$, and were conducted thus: First, pure, dry, gaseous hydrochloric acid was passed into a weighed absorption apparatus containing pure distilled water. After noting the increase in weight, gaseous ammonia was passed through to slight excess, and the apparatus was weighed again. The excess of ammonia was then measured by titration with standard hydrochloric acid. In weighing, the apparatus was tared by another as nearly like it as possible, containing the same amount of water. Three sets of weighings were made, with apparatus of different size, and these Thomsen considers separately, giving the greatest weight to the experiments involving the largest masses of material. The data are as follows, with the ratio $\frac{HCl}{NH_3}$ in the third column:

First Series.

Wt. HCl.	Wt. NH_3.	Ratio
5.1624	2.4120	2.1403
3.9425	1.8409	2.1416
4.6544	2.1739	2.1411
3.9840	1.8609	2.1409
5.3295	2.4898	2.1406
4.2517	1.9863	2.1405
4.8287	2.2550	2.1414
6.4377	3.0068	2.1411
4.1804	1.9528	2.1407
5.0363	2.3523	2.1410
4.6408	2.1685	2.1411

Second Series.

Wt. HCl.	Wt. NH_3.	Ratio.
11.8418	5.5302	2.14130
14.3018	6.6808	2.14073
12.1502	5.6759	2.14067
11.5443	5.3927	2.14073
12.3617	5.7733	2.14118

Third Series.

Wt. HCl.	Wt. NH_3.	Ratio.
19.3455	9.0360	2.14094
19.4578	9.0890	2.14081

[1] *Ztschr. phys. Chem.*, 13, 398.

From the sums of the weights Thomsen finds the ratio to be 2.14087, or 2.13934 in vacuo. From this, using Ostwald's reduction of Stas' data for the atomic weights of nitrogen and chlorine, he gets the ratio O : H : : 16 : 0.99946, or almost exactly 16 : 1. In a later paper[1] Thomsen himself recalculates Stas' data, with O = 16 as the basis of computation, and derives from them the subjoined values for the elements which Stas studied:

Ag	107.9299
Cl	35.4494
Br	79.9510
I	126.8556
S	32.0606
Pb	206.9042
K	39.1507
Na	23.0543
Li	7.0307
N	14.0396

Combining these values for chlorine and nitrogen with his ratio $HCl : NH_3$ he gets O : H : : 16 : 0.9992. This, however, is only an apparent support of Prout's hypothesis, for it depends upon the anti-Proutian determinations of Stas. If we calculate from Thomsen's new ratio with N = 14 and Cl = 35.5, it gives H = 1.0242; which is most unsatisfactory. In short, the method followed by Thomsen is too indirect and subject to too many possibilities of error to entitle it to much weight in fixing so important a constant as the atomic weight of oxygen. The direct processes, followed by several recent investigators, and giving O = 15.87 to 15.89 are much more trustworthy. Meyer and Seubert[2], in their criticism of Thomsen's work, have pointed out some of its uncertainties.

In this connection it may be noted that Scott's research upon the composition of water by volume, cited by abstract in the report of last year, has been published in full in the Philosophical Transactions.[3]

Strontium.—The atomic weight of strontium has been redetermined by Richards[4] from analyses of the bromide. The first ratio measured, after a careful preliminary study of materials

[1] *Ztschr. phys. Chem.*, 13, 726.
[2] *Ber d. chem. Ges.*, 27, 2770. See also abstract by Ostwald in *Ztschr. phys. Chem.*, 15, 705.
[3] 184, 543, *1893*.
[4] *Proc. Amer. Acad.* *1894*, 369.

and methods, was that between silver and strontium bromide. Of this ratio, three sets of determinations were made, all volumetric, but with differences of detail in the process. The weights are as follows, with the ratio $Ag_2 : SrBr_2 :: 100 : x$ in the third column:

FIRST SERIES.

Wt. Ag.	Wt. $SrBr_2$.	Ratio.
1.30755	1.49962	114.689
2.10351	2.41225	114.677
2.23357	2.56153	114.683
5.36840	6.15663	114.683
Sum, 11.01303	12.63003	114.683

SECOND SERIES.

Wt. Ag.	Wt. $SrBr_2$.	Ratio.
1.30762	1.49962	114.683
2.10322	2.41225	114.693
4.57502	5.24727	114.694
5.36800	6.15663	114.691
Sum, 13.35386	15.31577	114.692

THIRD SERIES.

Wt. Ag.	Wt. $SrBr_2$.	Ratio.
2.5434	2.9172	114.697
3.3957	3.8946	114.692
3.9607	4.5426	114.692
4.5750	5.2473	114.695
Sum, 14.4748	16.6017	114.694

From these data we have, if $Ag = 107.93$, and $Br = 79.955$, $(O = 16)$, the following results:

From first series..... $Sr = 87.644$
" second series..... 87.663
" third series..... 87.668

In two additional series, partly identical with the foregoing, the silver bromide thrown down was collected and weighed. I subjoin the weighings with the ratio $2AgBr : SrBr_2$ in the last column.

FIRST SERIES.

2AgBr.	$SrBr_2$.	Ratio.
2.4415	1.6086	65.886
2.8561	1.8817	65.884
6.9337	4.5681	65.883
Sum, 12.2313	8.0584	65.8834

SECOND SERIES.

2AgBr.	$SrBr_2$.	Ratio.
2.27625	1.49962	65.881
3.66140	2.41225	65.883
3.88776	2.56153	65.887
9.34497	6.15663	65.882
Sum, 19.17038	12.63003	65.883

From the first series..... Sr = 87.660
" " second series..... 87.659

The average of all five series is Sr = 87.659.

Barium.—Richards has corroborated his earlier determinations of the atomic weight of barium, which were made with the bromide, by means of additional series of experiments upon the chloride.[1] The work was carried out in the most elaborate and thorough manner, and for details the original paper must be consulted. First, barium chloride was titrated with standard solutions of silver, and the several series represent different methods of ascertaining accurately the end point. The data are as follows, with the ratio $Ag_2 : BaCl_2 :: 100 : x$ in the third column.

FIRST SERIES.

Wt. Ag.	Wt. $BaCl_2$.	Ratio.
6.1872	5.9717	96.517
5.6580	5.4597	96.495
3.5988	3.4728	96.499
9.4010	9.0726	96.507
0.7199	0.6950	96.541
		Mean, 96.512

SECOND SERIES.

Wt. Ag.	Wt. $BaCl_2$.	Ratio.
6.59993	6.36974	96.512
5.55229	5.36010	96.539
4.06380	3.92244	96.522
		Mean, 96.524

THIRD SERIES.

Wt. Ag.	Wt. $BaCl_2$.	Ratio.
4.4355	4.2815	96.528
2.7440	2.6488	96.531
6.1865	5.9712	96.520
3.4023	3.2841	96.526
		Mean, 96.526

[1] *Proc. Amer. Acad.*, 29, 55.

FOURTH SERIES.

Wt. Ag.	Wt. $BaCl_2$.	Ratio.
6.7342	6.50022	96.525
10.6023	10.23365	96.523
		Mean, 96.524

All the weights represent vacuum standards. From the four series the atomic weight of barium is deduced as follows; when O = 16.

First series	Ba = 137.419
Second "	" 137.445
Third "	" 137.449
Fourth "	" 137.445

In three more series of experiments Richards determined the ratio between 2AgCl and $BaCl_2$. The data are subjoined, with the ratio $2AgCl : BaCl_2 :: 100 : x$ appended.

FIRST SERIES.

Wt. AgCl.	Wt. $BaCl_2$.	Ratio.
8.7673	6.3697	72.653
5.1979	3.7765	72.654
4.9342	3.5846	72.648
2.0765	1.5085	72.646
4.4271	3.2163	72.650
		Mean, 72.649

SECOND SERIES.

Wt. AgCl.	Wt. $BaCl_2$.	Ratio.
2.09750	1.52384	72.650
7.37610	5.36010	72.669
5.39906	3.92244	72.650
		Mean, 72.6563

THIRD SERIES.

Wt. AgCl.	Wt. $BaCl_2$.	Ratio.
8.2189	5.97123	72.6524
4.5199	3.28410	72.6587
		Mean, 72.6555

Hence we have for Ba,

First series	Ba = 137.428
Second "	" = 137.446
Third "	" = 137.444

The mean of all is 137.440, as against 137.434 found in the work on the bromide. By combining the two chloride ratios,

$Ag_2 : BaCl_2$ and $2AgCl : BaCl_2$, the ratio Ag : Cl can be computed. This gives Ag = 107.930, a value identical with that of Stas.

Cobalt and Nickel.—The atomic weights of these two metals have been redetermined by Winkler,[1] who adopts a radically new method, using the pure electrolytic elements as a starting-point. In each case, the weighed metal, deposited upon platinum, is treated with a weighed excess of iodine dissolved in potassium iodide. The metals are thus converted into iodides, and the excess of iodine is then measured by titration with thiosulphate solution. Thus the direct ratios, Co : I, Ni : I, are determined. Two series of estimations are given for each metal, with results as follows. The atomic weights used in calculation are H = 1, I = 126.53.

FIRST SERIES—COBALT.

Wt. Co.	Wt. I.	At. Wt. Co.
0.4999	2.128837	59.4242
0.5084	2.166750	59.3772
0.5290	2.254335	59.3828
0.6822	2.908399	59.3582
0.6715	2.861617	59.3824
		Mean, 59.3849

SECOND SERIES—COBALT.

0.5185	2.209694	59.3798
0.5267	2.246037	59.3430
0.5319	2.268736	59.3294
		Mean, 59.3507

Mean of all, Co = 59.3678.

FIRST SERIES—NICKEL.

Wt. Ni.	Wt. I.	At. Wt. Ni.
0.5144	2.217494	58.6702
0.4983	2.148502	58.6918
0.5265	2.268742	58.7268
0.6889	2.970709	58.6828
0.6876	2.965918	58.6678
		Mean, 58.6878

SECOND SERIES—NICKEL.

0.5120	2.205627	58.7436
0.5200	2.204107	58.7432
0.5246	2.259925	58.7432
		Mean, 58.7433

[1] *Ztschr. anorg. Chem.*, **8**, 1.

Mean of all, Ni = 58.7155.

For O = 16, these become

Co = 59.517

Ni = 58.863.

Palladium—In 1889 Keiser published his determinations of the atomic weight of palladium, for which, since then, other investigators have found somewhat different values. He has now, jointly with Mary B. Breed, given a new set of determinations, which confirm his former series.[1] As before, palladiammonium chloride was reduced in hydrogen, the salt being prepared by two methods and carefully examined as to purity. Two series of experiments are given, with the following weights of material:

FIRST SERIES.

$Pd(NH_3Cl)_2$.	Pd.	At. Wt. Pd.
1.60842	0.80997	106.271
2.08295	1.04920	106.325
2.02440	1.01975	106.334
2.54810	1.28360	106.342
1.75505	0.88410	106.341
	From sum of weights,	106.325
	Reduced to vacuum,	106.246

SECOND SERIES.

$Pd(NH_3Cl)_2$.	Pd.	At. Wt. Pd.
1.50275	0.75685	106.297
1.23672	0.62286	106.296
1.34470	0.67739	106.343
1.49059	0.75095	106.353
	From sum of weights,	106.322
	Reduced to vacuum,	106.245

The atomic weight was computed with H = 1, N = 14.01, and Cl = 35.37. If O = 16 this becomes Pd = 106.51. This is only 0.02 less than the value obtained in the earlier investigation.

Tungsten.—A new determination of the atomic weight of tungsten, by Pennington and Smith,[2] leads to a much higher value than that commonly accepted. The older work seems very probably to have been done upon material contaminated

[1] *Am. Chem. J.*, 16, 20.

[2] Read before the Amer. Philos. Soc., Nov. 2, 1894.

with molybdenum, an impurity which was eliminated in this investigation by Debray's method,—that is, by volatilization by means of gaseous hydrochloric acid. The metal, carefully purified, was oxidized in porcelain crucibles, with all necessary precautions, and the following data are given:

Wt. W.	Wt. O_3.	At. Wt. W.
0.862871	0.223952	184.942
0.650700	0.168900	184.923
0.597654	0.155143	184.909
0.666820	0.173103	184.902
0.428228	0.111168	184.900
0.671920	0.174406	184.925
0.590220	0.153193	184.933
0.568654	0.147588	184.943
1.080973	0.280600	184.913
		Mean, 184.921

All weights are reduced to a vacuum, and O = 16 is taken as the standard of reference.

Another paper, by Smith and Desi, was read at the same meeting with that just cited. In this research, the tungstic oxide was purified in the same way, and reduced by heating in a stream of pure hydrogen. The water formed was weighed, and all weights reduced to a vacuum. Computed with O = 16 and H = 1.008, the results are as follows:

Wt. WO_3.	Wt. H_2O.	At. Wt. W.
0.983024	0.22834	184.683
0.998424	0.23189	184.709
1.008074	0.23409	184.749
0.911974	0.21184	184.678
0.997974	0.23179	184.704
1.007024	0.23389	184.706
		Mean, 184.704

Why this result should be lower than that previously found by Pennington and Smith remains to be explained.

Thallium.—Two determinations of atomic weight were made by Wells and Penfield to ascertain the constancy of the element as such.[1] The nitrate was fractionally crystallized until about one-twentieth remained in the mother-liquor, while another

[1] *Am. J. Sci.*, [3], 47, 466.

twentieth had been subjected to repeated recrystallization. Both fractions were converted into thallium chloride, which was dried at 100°, and in both the chlorine was estimated by weighing as silver chloride on a Gooch filter. The results were as follows:

	TlCl.	AgCl.	At. Wt. Tl.
Crystals	3.9146	2.3393	204.47
Mother-liquor	3.3415	1.9968	204.47

Calculated with Ag = 107.92 and Cl = 35.45.

In the report for 1893 Lepierre's work on thallium was given, and the last value cited was Tl = 203.00, varying widely from the rest of the series, and affecting the mean. The mean stated by Lepierre was 203.62, and as found by me was 203.57. Lepierre[1] now calls attention to the fact that his value 203.00 was a misprint for 203.60, and that his mean was therefore correctly given. He also gives additional details relative to his work.

Bismuth.—The long-standing controversy between Schneider and Classen over the atomic weight of bismuth, has led to a new set of determinations on the part of Schneider.[2] The old method was still used; namely, of converting the metal into the trioxide by means of nitric acid and subsequent ignition of the nitrate; but the metal itself was carefully purified. Results as follows:

Wt. Bi.	Wt. Bi_2O_3.	Per cent. Bi in Bi_2O_3.
5.0092	5.5868	89.661
3.6770	4.1016	89.648
7.2493	8.0854	89.659
9.2479	10.3142	89.662
6.0945	6.7979	89.653
12.1588	13.5610	89.660
		Mean, 89.657

If O = 16, Bi ranges from 207.94 to 208.15, or in mean 208.05, confirming the earlier determinations.

Tin.—Incidentally to his paper on the white tin sulphide Schmidt gives one determination of the atomic weight of the metal.[3]

0.5243 gram Sn gave 0.6659 SnO_2. Hence Sn = 118.48.

[1] *Bull. Soc. Chim.*, [3], 11, 423.
[2] *J. prakt. Chem.*, [2], 50, 461.
[3] *Ber d. chem. Ges.*, 27, 2743.

Anomalous Nitrogen.—An important discovery has been made by Lord Rayleigh, who finds that nitrogen obtained by purely chemical methods is perceptibly lighter than that from atmospheric air.[1] Equal volumes of the gas, variously prepared, weighed as follows:

By passing NO over hot iron	2.30008
" " N_2O " " "	2.29904
" " $AmNO_2$ " " "	2.29869

For nitrogen from air he found:

From air passed over hot iron	2.31003
" " " through moist FeO_2H_2	2.31020
" " " over hot copper	2.31026

Investigating the cause of this anomaly, with the co-operation of Ramsay, Rayleigh came to the astonishing results communicated a few months later to the British Association. It was found, in short, that atmospheric air contains a gas heavier than nitrogen, and hitherto unknown. Its density, in a sample as pure as could be obtained, was 19.09, and it was characterized by extraordinary inertness. Whether it is a new element, or allotropic nitrogen, N_3, remains to be determined. The work is cited here because it shows that the density of nitrogen as hitherto determined, can give no trustworthy value for the atomic weight of the element.

Miscellaneous Notes.—Some data bearing upon the atomic weight of tellurium are given by Gooch and Howland.[2] As the homogeneity of tellurium is still uncertain, I omit their details.

Wanklyn's attempt to show that the atomic weight of carbon is not 12, but 6, was noted last year. He has since published more on the subject in a paper on Russian Kerosene,[3] and the matter was also discussed at the Oxford meeting of the British Association.[4]

In a communication upon the Stasian determinations,[5] Hinrichs discusses the availability of silver as a secondary standard in the scale of atomic weights. He makes silver, chlorine, bromine, iodine, and sulphur all Proutian in value. Hinrichs also

[1] *Chem. News*, **69**, 231, May 18, *1894*.
[2] *Am. J. Sci.*, [3], **48**, 375.
[3] *Phil. Mag.*, [5], **37**, 495.
[4] *Chem. News*, **70**, 87, Aug. 24, *1894*.
[5] *Compt. rend.*, **118**, 528.

has published his views upon atomic weights *in extenso* in book form.[1]

In conclusion I submit a table of atomic weights revised to January 1, 1894. O = 16 is still retained as the base of the system; but I hope that in another year it will be practicable to return to H = 1.

Name.	Atomic Weight.	Name.	Atomic Weight.
Aluminum	27.	Neodymium	140.5
Antimony	120.	Nickel	58.7
Arsenic	75.	Nitrogen	14.03
Barium	137.43	Osmium	190.8
Bismuth	208.	Oxygen	16.
Boron	11.	Palladium	106.5
Bromine	79.95	Phosphorus	31.
Cadmium	112.	Platinum	195.
Caesium	132.9	Potassium	39.11
Calcium	40.	Praseodymium	143.5
Carbon	12.	Rhodium	103.
Cerium	140.2	Rubidium	85.5
Chlorine	35.45	Ruthenium	101.6
Chromium	52.1	Samarium	150.
Cobalt	59.5	Scandium	44.
Columbium	94.	Selenium	79.
Copper	63.6	Silicon	28.4
Erbium	166.3	Silver	107.92
Fluorine	19.	Sodium	23.05
Gadolinium	156.1	Strontium	87.66
Gallium	69.	Sulphur	32.06
Germanium	72.3	Tantalum	182.6
Glucinum	9.	Tellurium	125.
Gold	197.3	Terbium	160.
Hydrogen	1.008	Thallium	204.18
Indium	113.7	Thorium	232.6
Iodine	126.85	Thulium	170.7
Iridium	193.1	Tin	119.
Iron	56.	Titanium	48.
Lanthanum	138.2	Tungsten	184.9
Lead	206.95	Uranium	239.6
Lithium	7.02	Vanadium	51.4
Magnesium	24.3	Ytterbium	173.
Manganese	55.	Yttrium	89.1
Mercury	200.	Zinc	65.3
Molybdenum	96.	Zirconium	90.6

[1] The True Atomic Weight of the Chemical Elements, and the Unity of Matter. By Gustavus Detlef Hinrichs, St. Louis, 1894.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY, U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY, NO. 13.]

COLORING MATTER IN THE CALIFORNIA RED WINES.[1]

BY W. D. BIGELOW.

Received January 2, 1895.

DURING the last three quarters of a century the coloring matter of red wines has been carefully investigated. Those undertaking the work have endeavored to find some reaction or series of reactions, by which the natural coloring matter of the grape could be distinguished from that of other fruit and vegetables with which wines are so frequently adulterated. The introduction of the aniline colors into this industry attracted for a time a portion of the attention which had previously been given entirely to the vegetable colors, and methods have been brought forward by which the former can be recognized. On account of the comparative ease and certainty with which the aniline colors con be detected, wine makers still give their preference to the vegetable pigments, and a method for their detection is still regarded as desirable. A large number of methods have been suggested for this purpose, but most of them have proved worthless, and none of them at all satisfactory.

Among the difficulties which have been encountered by workers in this field, and which have not yet been overcome, are the following:

1. Many of the substances employed for coloring wines are so nearly identical with the natural coloring matter of the grape that it would not be an easy matter to distinguish between them even in freshly prepared solutions.

2. The coloring matter of wine changes materially with age, and different reactions are given by samples of the same variety and from the same locality, but of different vintages.

3. Different reactions are commonly obtained with wines of the same age, but of different varieties or from different parts of the country.

[1] Read before the Washington Section in abstract, November 8, 1894, and before the American Chemical Society, December 27, 1894.

As an example of the difficulties which are met with in making use of any of the methods that have been brought forward, let us notice the action of lead subacetate. According to Vögel this reagent gives a grayish green precipitate with pure wines, while with wines colored with elderberries, the juice of beets, &c., a precipitate colored indigo-blue, red, or some equally characteristic color is obtained. A more careful examination of the method revealed the fact that a number of fortified wines known to be free from foreign coloring matter gave distinct red and violet precipitates, while elderberries and mallow added to some of the lighter wines could not be detected. The same difficulties are experienced to a greater or less extent in all methods which have been suggested, and it is now customary in examining a wine for foreign vegetable coloring matter, to compare it with a wine of known purity, of the same variety, the same vintage, and from the same locality, as the sample under examination.

This work with California wines was done under the direction of Dr. H. W. Wiley, and was in connection with the examination made during the past year of the samples furnished by the California Viticultural Association. In all, ninety-four samples of California red wines were examined. Their age varied from one to seven years.

No wines were available which were known to be colored with vegetable pigments, and the facilities for coloring them were lacking, since wines colored after fermentation are quite different from those fermented after the addition of colored vegetable material to the must. This work was not undertaken, therefore, with the hope of developing a method for the detection of foreign coloring matter in wine, but merely for the purpose of studying the coloring matter of California wines, and of recording the reactions given by some of the reagents, whose reactions with the European wines have been the subject of so much careful study. The number of reagents employed was limited by the size of the samples.

For convenience the methods which were employed are divided into three classes. The methods given in the first class give a red, blue, or violet color with wines containing foreign

coloring matter, and usually a green or grayish green tint when the wines are pure.

The second class of reagents includes certain metallic oxides, such as manganese dioxide and lead dioxide. These have been used in different proportions, sometimes to distinguish between natural wines and those colored with foreign vegetable colors, sometimes between the vegetable colors and coal-tar colors in wine. They have not been found entirely satisfactory, since the amount necessary to decolorize some pure wines is sufficient to destroy even the aniline colors in some that had been artificially colored. Yet they have been found of great assistance in the examination of such wines as claret and burgundy. These reagents were found to destroy almost all the color in California wines when used in the proportions recommended for French claret and similar wines.

The third class includes methods which use chalk treated with albumen and charged with varions reagents.

CLASS 1.

Lead Acetate—Neutral and Basic.—The reactions obtained with neutral and basic lead acetate were almost identical. The precipitates were yellowish green, grayish green, gray or brown. No blue, red, or violet colors were obtained.

Sodium Carbonate.—In the use of this reagent the solution recommended by Gautier (Sophistication et analyse des vins, 4me. edition, page 211) was employed. One cc. of wine was mixed with five cc. of a five-tenths per cent. solution of sodium carbonate. The colors obtained were brown, yellowish brown, and yellowish to grayish green.

Sodium Bicarbonate.—Gautier's solution was also employed with this reagent. Eight grams of sodium bicarbonate were dissolved in 100 cc. of water and the solution saturated with carbon dioxide. Equal volumes of this solution and the wine under examination were mixed and the color noted. The reactions obtained were gray or grayish green, with sometimes a tinge of brown.

Ammonia.—The action of dilute ammonia on red wine was first pointed out by Chevallier in 1827, and since then it has been commonly used in their examination. The solution used in this

work contained one part of strong ammonia to nine parts of water. This was then added to wine in equal volumes, and the resulting mixture was filtered when turbid. The filtrates were colored various shades of brown and green with an occasional orange-red.

Ammonium Hydroxide and Ammonium Sulphhydroxide.—A mixture of twenty cc. of ammonium hydroxide and eight cc. of ammonium sulphhydroxide were diluted with water to one liter, and a portion of five cc. treated with an equal volume of wine. The resulting solutions were brown to yellowish brown.

Alum and Potassium Carbonate.—Five cc. of a saturated solution of ammonia alum were mixed with ten cc. of wine, five cc. of a one-tenth solution of potassium carbonate added, and the whole stirred and filtered. The precipitates were gray or yellowish brown with sometimes a tinge of green. The filtrates were sometimes of a light wine color, but were not lilac or wine-colored in any case.

Alum and Lead Acetate.—This method is the same as the preceding except that a one-tenth solution of lead acetate is used instead of potassium carbonate. The precipitates were colored yellowish gray to brown except in three cases, when they were of a light wine color.

Borax.—Two volumes of a saturated solution of borax were mixed with one of wine. A brown to yellowish brown color was obtained with all wines except one sample of Gutedel, which gave an orange-red color.

Copper Sulphate.—Ten cc. of wine were diluted with water to 100 cc. and thirty cc. of a saturated solution of copper sulphate added. The color of the solution was changed in every case to a light olive-green.

Tartar Emetic.—Two to three volumes of wine were mixed with one volume of a saturated solution of tartar emetic. The color was changed in every case to a bright cherry-red.

CLASS 2.

Manganese Dioxide.—100 cc. of wine were shaken for fifteen minutes with fifteen grams of manganese dioxide, and the mixture filtered. The filtrates were light colored, but were not entirely decolorized in any case. Shaking the filtrates with

another portion of fifteen grams of maganese dioxide rendered them almost colorless.

Lead Peroxide.—Five grams of lead peroxide were added to twenty cc. of wine, and the mixture well shaken and filtered. Some of the filtrates were entirely decolorized, though in many of them a very light wine color remained.

Mercuric Oxide.—Ten cc. of wine were shaken for one minute with three-tenths to four-tenths gram precipitated mercuric oxide (Cazeneuve uses one to one and one-half grams) and filtered. The filtrates were all colorless or light yellow.

CLASS 3.

Sodium Peroxide.—M. Ruisand uses sodium peroxide to detect aniline coloring matters in wine. He adds ten to fifteen cc. of sodium peroxide to five cc. of wine, allows it to stand twenty minutes, and renders slightly acid with acetic acid. According to Ruisand, both vegetable colors and aniline derivatives are decolorized by the peroxide, while the coal-tar colors are restored by acetic acid.

With the California wines the color is not entirely destroyed, even with twice the quantity of peroxide recommended by Ruisand, and in many cases a marked wine color remained both before and after acidification.

A lump of chalk was cut into pieces about fifteen mm. square and half as thick, and one side of each piece was carefully smoothed with a knife. These pieces of chalk were then immersed for two hours in a ten per cent. solution of egg albumen and dried at 45°. They were then divided into five portions, one of which was reserved for testing the wine without further treatment, and each of the other four immersed for forty minutes in a one per cent. solution of one of the following reagents: Tartar emetic, lead acetate, copper acetate, and zinc acetate. After being dried at 50°, they are ready for use. Three drops of each wine examined were placed on the smooth surface of one block from each of the five divisions given above, the blocks dried at 100° for one hour, and the color noted. Another block from each division was treated with the same amount of wine, dried for twenty-four hours at the temperature of the laboratory, and the color compared with that of the blocks dried at 100°. The colors

obtained were brown, grayish brown, and slate colored. No tinge of violet, blue, or green, was obtained in any case. In every case the color of the block dried at 100° was almost, if not exactly, identical with that of the block treated with the same wine and dried at the temperature of the laboratory.

According to the reactions obtained with these reagents, the coloring matter of California wines appears to be much more uniform than that of European wines. The reactions are not always the same as those obtained with the more ordinary European wines; for instance, a gray, or yellowish, or orange-gray precipitate or solution is sometimes obtained with reagents which are said to give green or grayish green with French wines. On the other hand no reactions were obtained which are said to be characteristic of wines colored with vegetable pigments.

THE PENETRATION MACHINE—AN EXPLANATION.

By H. C. Bowen.

Received January 24, 1895.

ON page 59, January number, 1895, of this JOURNAL, a somewhat vague reference is made to a testing instrument. The identity of the instrument referred to is made manifest to me by the context. The instrument is known by those who have to do with it as the Penetration Machine; first described in print by myself in the School of Mines Quarterly, **10,** 297, under the title "An Apparatus for Determining the Relative Degree of Cohesion of a Semi-Liquid Body." The reference above noted, by some mischance, does the instrument and its work injustice. The origin of the instrument was due to pressing needs in the technology of alsphalt cements used for paving purposes. These cements, made by different parties using different tempering agents, were very varied, and at the time of the origin of this instrument there was no way other than chewing the cement for foremen to test whether the cement was of required consistency or not. Since that time (1889) thousands of tons of cement have been manufactured, and the whole of this cement has been strictly tested by this machine with nicety and satisfaction. These cements are made in all parts of the country, to a certain penetration number, previously determined as necessary according to the different uses of the cement.

Without this control cements would be used that were not suited for the purpose designed, and much damage would be occasioned in different cities, which damage would much cripple the asphalt paving industry. Cargoes of cement are shipped, one requirement of the cement being that it shall have a certain penetration number previously determined by the contracting parties. Since the introduction of this testing apparatus many qualities of cement have been studied and others discovered. By it we have learned the influence of mild or sudden and marked changes of temperatures, and the consequence of severe cold. It enables us to learn the influence of hardening and softening agents, a matter of great importance in the practical uses of asphalt cement. Thus it is manifest that this instrument has an important and serious part to perform in a great industry, and that its use is far from being an idle pastime.

SCHOOL OF MINES, COLUMBIA COLLEGE,
N. Y. CITY, January 23, 1895.

NOTES.

Argon: A New Constituent of the Atmosphere.—At the meeting of the Royal Society, held on January 31, the long-expected paper by Lord Rayleigh and Professor Ramsay was read, and a full report has just been received by way of *The Chemical News*, of February 1, from which the following condensed summary is taken: A careful comparison of the nitrogen from urea, ammonium nitrite, and from nitrous and nitric oxid—"chemical nitrogen" with atmospheric nitrogen was made, and gave a weight per liter for

Chemical nitrogen of.....	1.2505 grams
Atmospheric "	1.2572 "

Nitrogen which had been extracted from the air by means of magnesium was separated also and gave a figure differing inappreciably from that recorded above for "chemical nitrogen."[1] The nitrogen contained in magnesium nitride was also converted into ammonium chloride and this was found to contain exactly the proportion of chlorine contained in ordinary ammonium chloride. From this it was concluded that red-hot magnesium withdraws from "atmospheric nitrogen" no substance other than nitrogen capable of forming a basic compound with hydrogen. After having endeavored in every way possible to detect in "atmospheric nitrogen" known gases to account for the difference in specific gravity the authors finally repeated Cavendish's experiment. It will be remembered that Cavendish found that when air to which oxygen was added, the electric spark passed for several days and the nitrous and nitric acids

[1] See also page 211 of this issue.

removed by soap-lees and finally the oxygen removed by liver of sulphur that "only a small bubble of air remained unabsorbed which certainly was not more than the $\frac{1}{120}$ of the bulk of the phlogisticated air let up into the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest and can not be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{120}$ part of the whole." Improving the apparatus of Cavendish so as to shorten the duration of the experiment Rayleigh and Ramsay found that fifty cc. of air left 0.32 cc. of gas. On adding this residue to a fresh fifty cc. of air and repeating the operation the residue now amounted to 0.76 cc.

By passing nitrogen over magnesium turnings contained in a heated tube, 1,500 cc. unabsorbed gas was obtained and after passing this for several days over soda-lime, phosphoric anhydride, magnesium at a red heat, and copper oxide, the gas was reduced to 200 cc. and its density found to be 16.1. After further absorption the density was increased to 19.09. On passing sparks for several hours through a mixture of a small quantity of this gas with oxygen, its volume was still further reduced. Assuming that this reduction was due to the further elimination of nitrogen the density of the remaining gas was calculated to be 20.0.

By means of atmolysis using long clay pipe-stems the amount of argon was increased in the air, which finally passed from the pipes so that the nitrogen in it weighed in a total weight of approximately two and three-tenths grams a mean of 0.00187 gram over that of the same volume of "atmospheric nitrogen." By increasing the efficiency of the apparatus the excess was in mean 0.0035 gram.

Experiments then made to prove the absence or presence of argon in chemical nitrogen showed that three liters of chemical nitrogen from ammonium nitrite left three and three-tenths cc. of argon, a part of which is accounted for by an accident. In a second experiment 5,660 cc. of the same nitrogen left three and five-tenths cc. argon. The source of this was found in the water used for confining the gases which absorbs argon from the air in considerable amount, and again gives it up to the confined gases. The amount of argon obtained from the chemical nitrogen was less than $\frac{1}{40}$ of the normal amount from atmospheric nitrogen. The following quotations from the paper of Rayleigh and Ramsay and from those of Crookes and Olszewski, which followed it, are scarcely susceptible of condensation:

Separation of Argon on a Large Scale.

To prepare argon on a large scale, air is freed from oxygen by means of red-hot copper. The residue is then passed from a gas-holder through a combustion tube, heated in a furnace, and containing copper, in order to remove all traces of oxygen; the issuing gas is then dried by passage over soda-lime and phosphorus pentoxide, after passage through a small U tube containing sulphuric acid, to indicate the rate of flow. It then enters a combustion tube packed tightly with magnesium turnings, and heated

to redness in a second furnace. From this tube it passes through a second index-tube, and enters a small gas-holder capable of containing three or four liters. A single tube of magnesium will absorb from seven to eight liters of nitrogen. The temperature must be nearly that of the fusion of the glass, and the current of gas must be carefully regulated, else the heat developed by the union of the magnesium with nitrogen will fuse the tube.

Having collected the residue from 100 to 150 liters of atmospheric nitrogen, which may amount to four or five liters, it is transferred to a small gas-holder connected with an apparatus, whereby, by means of a species of a self-acting Sprengel's pump, the gas is caused to circulate through a tube half filled with copper and half with copper oxide; it then traverses a tube half filled with soda-lime and half with phosphorus pentoxide; it then passes a reservoir of about 300 cc. capacity, from which, by raising a mercury reservoir, it can be expelled into a small gas-holder. Next it passes through a tube containing magnesium turnings heated to bright redness. The gas is thus freed from any possible contamination with oxygen, hydrogen, or hydrocarbons, and nitrogen is gradually absorbed. As the amount of gas in the tubes and reservoir diminishes in volume it draws supplies from the gas-holder, and, finally, the circulating system is full of argon in a pure state. The circulating system of tubes is connected with a mercury pump, so that, in changing the magnesium tube, no gas may be lost. Before ceasing to heat the magnesium tube the system is pumped empty, and the collected gas is restored to the gas-holder; finally, all the argon is transferred from the mercury reservoir to the second small gas-holder, which should preferably be filled with water saturated with argon, so as to prevent contamination from oxygen or nitrogen; or, if preferred, a mercury gas-holder may be employed. The complete removal of nitrogen from argon is very slow towards the end, but circulation for a couple of days usually effects it.

The principal objection to the oxygen method of isolating argon, as hitherto described, is the extreme slowness of the operation. In extending the scale we had the great advantage of the advice of Mr. Crookes, who not long since called attention to the flame rising from platinum terminals, which convey a high tension alternating electric discharge, and pointed out its dependence upon combustion of the nitrogen and oxygen of the air.[1] The plant consists of a De Meritens alternator, actuated by a gas engine, and the currents are transformed to a high potential by means of a Ruhmkorff or other suitable induction coil. The highest rate of absorption of the mixed gases yet attained is three liters per hour, about 3,000 times that of Cavendish. It is necessary to keep the apparatus cool, and from this and other causes a good many difficulties have been encountered.

In one experiment of this kind, the total air led in after seven days' working, amounted to 7,925 cc., and of oxygen (prepared from potassium

[1] *Chemical News*, 65, 301, *1892*.

chlorate), 9137 cc. On the eighth and ninth days oxygen alone was added, of which about 500 cc. was consumed, while there remained about 700 cc. in the flask. Hence the proportion in which the air and oxygen combined was as 79 : 96. The progress of the removal of the nitrogen was examined from time to time with the spectroscope, and became ultimately very slow. At last the yellow line disappeared, the contraction having apparently stopped for two hours. It is worthy of notice that with the removal of the nitrogen, the arc discharge changes greatly in appearance, becoming narrower and blue rather than greenish in color.

The final treatment of the residual 700 cc. of gas was on the model of the small scale operations, already described. Oxygen or hydrogen could be supplied, at pleasure, from an electrolytic apparatus, but in no way could the volume be reduced below sixty-five cc. This residue refused oxidation and showed no trace of the yellow line of nitrogen, even under favorable conditions.

When the gas stood for some days over water, the nitrogen line reasserted itself in the spectrum, and many hour's sparking with a little oxygen was required again to get rid of it. Intentional additions of air to gas free from nitrogen showed that about one and one-half per cent. was clearly, and about three per cent. was conspicuously, visible. About the same numbers apply to the visibility of nitrogen in oxygen when sparked under these conditions, that is, at atmospheric pressure, and with a jar connected to the secondary terminals.

Density of Argon prepared by means of Oxygen.

A first estimate of the density of argon prepared by the oxygen method was founded upon the data already recorded respecting the volume present in air, on the assumption that the accurately known densities of atmospheric and of chemical nitrogen differ on account of the presence of argon in the former, and that during the treatment with oxygen nothing is oxidized except nitrogen. Thus, if

D = density of chemical nitrogen,
D' = " " atmospheric nitrogen,
d = " " argon,
a = proportional volume of argon in atmospheric nitrogen,

the law of mixtures give—

$$ad + (1-a)D = D',$$

or—

$$d = D + (D'-D)/a.$$

In this formula $D' - D$ and a are both small, but they are known with fair accuracy, From the data already given—

$$a = \frac{65}{0.79 \times 7925}$$

whence if (on an arbitrary scale of reckoning) $D = 2.2990$, $D' = 2.3102$, we find $d = 3.378$. Thus if N_2 be 14, or O_2 be 16, the density of argon is 20.6.

A direct determination by weighing is desirable, but hitherto it has not

been feasible to collect by this means sufficient to fill the large globe employed for other gases. A *mixture* of about 400 cc. of argon with pure oxygen, however, gave the weight 2.7315, 0.1045 in excess of the weight of oxygen, *viz.*, 2.6270. Thus, if a be the ratio of the volume of argon to the whole volume, the number for argon will be—

$$2.6270 + 0.1045/a.$$

The value of a, being involved only in the excess of weight above that of oxygen, does not require to be known very accurately. Sufficiently concordant analyses by two methods gave $a = 0.1845$; whence for the weight of the gas we get 3.193, so that, if $O_2 = 16$, the density of the gas would be 19.45. An allowance for residual nitrogen, still visible in the gas before admixture of oxygen, raises this number to 19.7, which may be taken as the density of pure argon resulting from this determination.

Density of Argon prepared by means of Magnesium.

The density of the original sample of argon prepared has already been mentioned. It was 19.09; and, after sparking with oxygen, it was calculated to be 20.0. The most reliable results of a number of determinations give it as 19.90. The difficulty in accurately determining the density is to make sure that all nitrogen has been removed. The sample of density 19.90 showed no spectrum of nitrogen when examined in a vacuum tube. It is right, however, to remark that the highest density registered was 20.38. But there is some reason here to distrust the weighing of the vacuous globe.

Spectrum of Argon.

The spectrum of argon, seen in a vacuum tube of about three mm. pressure consists of a great number of lines, distributed over almost the whole visible field. Two lines are specially characteristic; they are less refrangible than the red lines of hydrogen or lithium, and serve well to identify the gas, when examined in this way. Mr. Crookes, who will give a full account of the spectrum in a separate communication, has kindly furnished us with the accurate wave-lengths of these lines, as well as of some others next to be described; they are respectively 696.56 and 705.64, 10^{-6} mm.

Besides these red lines, a bright yellow line, more refrangible than the sodium line, occurs at 603.84. A group of five bright green lines occurs next, besides a number of less intensity. Of the group of five, the second, which is perhaps the most brilliant, has the wave-length 561.00. There is next a blue or blue violet line of wave-length 470.2; and last, in the less easily visible part of the spectrum, there are five strong violet lines, of which the fourth, which is the most brilliant, has the wave-length 420.0.

Unfortunately, the red lines, which are not to be mistaken for those of any other substance, are not easily seen when a jar discharge is passed through argon at atmospheric pressure. The spectrum seen under these conditions has been examined by Professor Schuster. The most charac-

teristic lines are perhaps those in the neighborhood of F, and are very easily seen if there be not too much nitrogen, in spite of the presence of some oxygen and water vapor. The approximate wave-lengths are—

487.91	Strong.
[486.07]	F.
484.71	Not quite so strong.
480.52	Strong.
476.50	Fairly strong characteristic triplet.
473.53	
472.56	

It is necessary to anticipate Mr. Crookes' communication, and to state that when the current is passed from the induction coil in one direction, that end of the capillary tube next the positive pole appears of a redder, and that next the negative pole of a bluer hue. There are, in effect, two spectra, which Mr. Crookes has succeeded in separating to a considerable extent. Mr. E. C. Baly,[1] who has noticed a similar phenomenon, attributes it to the presence of two gases. He says: "When an electric current is passed through a mixture of two gases, one is separated from the other and appears in the negative glow." The conclusion would follow that what we have termed "argon" is in reality a mixture of two gases which have as yet not been separated. This conclusion, if true, is of great importance, and experiments are now in progress to test it by the use of other physical methods. The full bearing of this possibility will appear later.

The presence of a small quantity of nitrogen interferes greatly with the argon spectrum. But we have found that in a tube with platinum electrodes, after the discharge has been passed for four hours, the spectrum of nitrogen disappears, and the argon spectrum manifests itself in full purity. A specially constructed tube with magnesium electrodes, which we hoped would yield good results, removed all traces of nitrogen, it is true; but hydrogen was evolved from the magnesium, and showed its characteristic lines very strongly. However, these are easily identified. The gas evolved on heating magnesium *in vacuo*, as proved by a separate experiment, consists entirely of hydrogen.

Mr. Crookes has proved the identity of the chief lines of the spectrum of gas separated from air-nitrogen by aid of magnesium with that remaining after sparking the air-nitrogen with oxygen in presence of caustic soda solution.

Prof. Schuster has also found the principal lines identical in the spectra of the two gases, as observed by the jar discharge at atmospheric pressure.

Solubility of Argon in Water.

Determinations of the solubility in water of argon prepared by sparking, gave 3.94 volumes per 100 of water at 12°. The solubility of gas pre-

[1] *Proc. Phys. Soc.*, 1893, p. 147.

pared by means of magnesium was found to be 4.05 volumes per 100 at 13.9°. The gas is therefore about two and one-half times as soluble as nitrogen, and possesses approximately the same solubility as oxygen.

The fact that argon is more soluble than nitrogen would lead us to expect it in increased proportion in the dissolved gases of rain-water. Experiment has confirmed this anticipation. "Nitrogen" prepared from the dissolved gases of water supplied from a rain-water cistern was weighed upon two occasions. The weights, corresponding to those recorded * * were 2.3221 and 2.3227, showing an excess of twenty-four mgms. above the weight of true nitrogen. Since the corresponding excess for "atmospheric nitrogen" is eleven mgms. we conclude that the water "nitrogen" is relatively more than twice as rich in argon.

On the other hand, gas evolved from the hot spring at Bath, and collected for us by Dr. A. Richardson, gave a residue after removal of oxygen and carbon dioxide, whose weight was only about midway between that of true and atmospheric nitrogen.

Behavior at Low Temperatures.[1]

Preliminary experiments, carried out to liquefy argon at a pressure of about 100 atmospheres, and at a temperature of —90°, failed. No appearance of liquefaction could be observed.

Professor Charles Olszewski, of Cracow, the well-known authority on the constants of liquefied gases at low temperatures, kindly offered to make experiments on the liquefaction of argon. His results are embodied in a separate communication, but it is allowable to state here that the gas has a lower critical-point and a lower boiling-point than oxygen, and that he has succeeded in solidifying argon to white crystals. The sample of gas he experimented with was exceptionally pure, and had been prepared by help of magnesium. It showed no trace of nitrogen when examined in a vacuum tube.

Ratio of Specific Heats.

In order to decide regarding the elementary or compound nature of argon, experiments were made on the velocity of sound in it. It will be remembered that, from the velocity of sound in a gas, the ratio of specific heat at constant pressure to that at constant volume can be deduced by means of the equation—

$$n\lambda = v = \sqrt{\left\{\frac{e}{d}(1+at)\frac{C_p}{C_v}\right\}},$$

when n is the frequency, λ the wave-length of sound, v its velocity, e the isothermal elasticity, d the density, $(1+at)$ the temperature correction, C_p the specific heat at constant pressure, and C_v that at constant volume. In comparing two gases at the same temperature, each of which obeys Boyle's law with sufficient approximation, and in using the same sound,

[1] The arrangements for the experiments upon this branch of the subject were left entirely in Professor Ramsay's hands.

many of these terms disappear, and the ratio of specific heats of one gas may be deduced from that of the other, if known, by means of the proportion—

$$\lambda^2 d : \lambda'^2 d' :: 1.41 : x,$$

where, for example, λ and d refer to air, of which the ratio is 1.41, according to observations by Röntgen, Wüllner, Kayser, and Jamin and Richard.

Two completely different series of observations, one in a tube of about two mm. diameter, and one in one of eight mm., made with entirely different samples of gas, gave, the first, 1.65 as the ratio, and, the second, 1.61.

Experiments made with the first tube, to test the accuracy of its working, gave for carbon dioxide the ratio 1.276, instead of 1.288, the mean of all previous determinations; and the half wave-length of sound in hydrogen was found to be 73.6, instead of 74.5, the mean of those previously found. The ratio of the specific heats of hydrogen found was 1.39, instead of 1.402.

There can be no doubt, therefore, that argon gives practically the ratio of specific heats, *viz.*, 1.66 proper to a gas in which all the energy is translational. The only other gas which has been found to behave similarly is mercury gas, at a high temperature.[1]

Attempts to Induce Chemical Combination.

Many attempts to induce argon to combine will be described in full in the complete paper. Suffice it to say here that all such attempts have as yet proved abortive. Argon does not combine with oxygen in presence of alkali under the influence of the electric discharge, nor with hydrogen in presence of acid or alkali also when sparked; nor with chlorine, dry or moist, when sparked; nor with phosphorus at a bright-red heat; nor with sulphur at bright redness. Tellurium may be distilled in a current of the gas; so may sodium and potassium, their metallic luster remaining unchanged. It is unabsorbed by passing it over fused red-hot caustic soda, or soda-lime heated to bright redness; it passes unaffected over fused and bright red-hot potassium nitrate; and red-hot sodium peroxide does not combine with it. Persulphides of sodium and calcium are also without action at a red heat. Platinum-black does not absorb it, nor does platinum sponge, and wet oxidizing and chlorinating agents, such as nitrohydrochloric acid, bromine water, bromine and alkali, and hydrochloric acid and potassium permanganate, are entirely without action. Experiments with fluorine are in contemplation, but the difficulty is great; and an attempt will be made to produce a carbon arc in the gas. Mixtures of sodium and silica and of sodium and boracic anhydride are also without action; hence it appears to resist attack by nascent silicon and by nascent boron.

General Conclusions.

It remains, finally, to discuss the probable nature of the gas, or mix-

[1] Kundt and Warburg, *Pogg. Ann.*, 135, 337 and 527.

ture of gases, which we have succeeded in separating from atmospheric air, and which we provisionally name *argon*.

The presence of argon in the atmosphere is proved by many lines of evidence. The high density of "atmospheric nitrogen," the lower density of nitrogen from chemical sources, and the uniformity in the density of samples of chemical nitrogen prepared from different compounds, lead to the conclusion that the cause of the anomaly is the presence of a heavy gas in air. If that gas possess the density twenty compared with hydrogen, "atmospheric" nitrogen should contain of it approximately one per cent. This is, in fact, found to be the case. Moreover, as nitrogen is removed from air by means of red-hot magnesium, the density of the remaining gas rises proportionately to the concentration of the heavier constituent.

Second.—This gas has been concentrated in the atmosphere by diffusion. It is true that it has not been freed from oxygen and nitrogen by diffusion, but the process of diffusion increases, relatively to nitrogen, the amount of argon in that portion which does not pass through the porous walls. This has been proved by its increase in density.

Third.—As the solubility of argon in water is relatively high, it is to be expected that the density of the mixture of argon and nitrogen, pumped out of water along with oxygen, should, after the removal of the oxygen, be higher than that of "atmospheric" nitrogen. Experiment has shown that the density is considerably increased.

Fourth.—It is in the highest degree improbable that two processes, so different from each other, should manufacture the same product. The explanation is simple if it be granted that these processes merely eliminate nitrogen from an "atmospheric" mixture. Moreover, as argon is an element, or a mixture of elements, its manufacture would mean its separation from one of the substances employed. The gas which can be removed from red-hot magnesium in a vacuum has been found to be wholly hydrogen. Nitrogen from chemical sources has been practically all absorbed by magnesium, and also when sparked in presence of oxygen; hence, argon can not have resulted from the decomposition of nitrogen. That it is not produced from oxygen is sufficiently borne out by its preparation by means of magnesium.

Other arguments could be adduced, but the above are sufficient to justify the conclusion that argon is present in the atmosphere.

The identity of the leading lines in the spectrum, the similar solubility and the similar density, appear to prove the identity of the argon prepared by both processes.

Argon is an element, or a mixture of elements, for Clausius has shown that if K be the energy of translatory motion of the molecules of a gas, and H their whole kinetic energy, then—

$$\frac{K}{H} = \frac{3(C_p - C_v)}{2C_v}$$

C_p and C_v denoting as usual the specific heat at constant pressure and at

constant volume respectively. Hence if, as for mercury vapor and for argon, the ratio of specific heats $C_p : C_v$ be $1\frac{2}{3}$, it follows that K = H, or that the whole kinetic energy of the gas is accounted for by the translatory motion of its molecules. In the case of mercury, the absence of interatomic energy is regarded as proof of the monatomic character of the vapor, and the conclusion holds equally good for argon.

The only alternative is to suppose that if argon molecules are di- or polyatomic, the atoms acquire no relative motion, even of rotation, a conclusion exeeedingly improbable in itself, and one postulating the sphericity of such complex groups of atoms.

Now a monatomic gas can be only an element, or a mixture of elements; and hence, it follows that argon is not of a compound nature.

From Avogadro's law, the density of a gas is half its molecular weight; and as the density of argon is approximately twenty, hence, its molecular weight must be forty. But its molecule is identical with its atom; hence, its atomic weight, or, if it be a mixture, the mean of the atomic weights of that mixture, taken for the proportion in which they are present, must be forty.

There is evidence both for and against the hypothesis that argon is a mixture; for, owing to Mr Crooke's observations of the dual character of its spectrum; against, because of Professor Olszewski's statement that it has a definite melting-point, a definite boiling-point, and a definite critical temperature and pressure; and because, on compressing the gas in presence of its liquid, pressure remains sensibly constant until all gas has condensed to liquid. The latter experiments are the well-known criteria of a pure substance; the former is not known with certainty to be characteristic of a mixture. The conclusions which follow are, however, so startling that in our future experimental work we shall endeavor to decide the question by other means.

For the present, however, the balance of evidence seems to point to simplicity. We have, therefore, to discuss the relations to other elements of an element of atomic weight forty. We inclined for long to the view that argon was possibly one or more than one of the elements which might be expected to follow fluorine in the periodic classification of the elements—elements which should have an atomic weight between nineteen, that of fluorine, and twenty-three, that of sodium. But this view is completely put out of court by the discovery of the monatomic nature of its molecules.

The series of elements possessing atomic weights near forty are—

Chlorine	35.5
Potassium	39.1
Calcium	40.0
Scandium	44.0

There can be no doubt that potassium, calcium, and scandium follow legitimately their predecessors in the vertical columns, lithium, beryllium,

and boron, and that they are in almost certain relation with rubidium, strontium, and (but not so certainly) yttrium. If argon be a single element, then there is reason to doubt whether the periodic classification of the elements is complete; whether, in fact, elements may not exist which can not be fitted among those of which it is composed. On the other hand, if argon be a mixture of two elements, they might find place in the eighth group, one after chlorine and one after bromine. Assuming thirty-seven (the approximate mean between the atomic weights of chlorine and potassium) to be the atomic weight of the lighter element, and forty the mean atomic weight found, and supposing that the second element has an atomic weight between those of bromine, eighty, and rubidium, 85.5; *viz.*, eighty-two, the mixture should consist of 93.3 per cent. of the lighter, and six and seven-tenths per cent. of the heavier element. But it appears improbable that such a high percentage as six and seven-tenths of heavier element should have escaped detection during liquefaction.

If it be supposed that argon belongs to the eighth group, then its properties would fit fairly well with what might be anticipated. For the series, which contains—

$$Si_{N}^{\text{IV.}},\ P_{4}^{\text{III. and V.}},\ S_{8\text{ to }2}^{\text{II. to VI.}},\ \text{and}\ Cl_{2}^{\text{I. to VII.}},$$

might be expected to end with an element of monatomic molecules of no valency, *i. e.*, incapable of forming a compound, or if forming one, being an octad; and it would form a possible transition to potassium, with its monovalence, on the other hand. Such conceptions are, however, of a speculative nature; yet they may be, perhaps, excused, if they, in any way lead to experiments which tend to throw more light on the anomalies of this curious element.

In conclusion, it need excite no astonishment that argon is so indifferent to reagents. For mercury, although a monatomic element, forms compounds which are by no means stable at a high temperature in the gaseous state; and attempts to produce compounds of argon may be likened to attempts to cause combination between mercury gas at 800° and other elements. As for the physical condition of argon, that of a gas, we possess no knowledge why carbon, with its low atomic weight, should be a solid, while nitrogen is a gas, except in so far as we ascribe molecular complexity to the former and comparative molecular simplicity to the latter. Argon, with its comparatively low density and its molecular simplicity, might well be expected to rank among the gases. And its inertness, which has suggested its name, sufficiently explains why it has not previously been discovered as a constituent of compound bodies.

We would suggest for this element, assuming provisionally that it is not a mixture, the symbol A.

We have to record our thanks to Messrs. Gordon, Kallas, and Matthews, who have materially assisted us in the prosecution of this research.

Mr. Crookes (before reading his paper) said: Allow me, Mr. President, to take this opportunity of striking the key-note of the chorus of applause

and congratulations which will follow from all chemists present on this most valuable and important paper. The difficulties in a research of this kind are peculiar. Here we have a new chemical element, the principal properties of which seem to be the negation of all chemical properties. Chemists will understand how difficult it is to deal with anything which forms no compounds and unites with nothing. The discovery commenced by a prediction, followed after an interval by realization. Discoveries of this kind are more important and take a higher rank, than discoveries which, more or less, come in a haphazard sort of way. The prediction and discovery of argon are only equalled by the few discoveries of elements which have been made in chemistry by the careful study of the periodic law, and to surpass it we must go back to the predicted existence and subsequent discovery of an unknown planet by Adams and Leverrier.

On the Spectra of Argon. By William Crookes, F. R. S., etc. (Abstract.)

Through the kindness of Lord Rayleigh and Professor Ramsay I have been enabled to examine the spectrum of this gas in a very accurate spectroscope, and also to take photographs of its spectra in a spectrograph fitted with a complete quartz train.

Argon resembles nitrogen in that it gives two distinct spectra, according to the strength of the induction current employed. But while the two spectra of nitrogen are different in character, one showing fluted bands and the other sharp lines, the argon spectra both consist of sharp lines. It is, however, very difficult to get argon so free from nitrogen that it will not at first show the nitrogen flutings superposed on its own special system of lines. I have used argon prepared by Lord Rayleigh, Professor Ramsay, and myself, and however free it was supposed to be from nitrogen, I could always detect the nitrogen bands in its spectrum. These, however, soon disappear when the induction spark is passed through the tube for some time, varying from a few minutes to a few hours. The vacuum tubes best adapted for showing the spectra are of the ordinary Plücker form, having a capillary tube in the middle. For photographing the higher rays which are cut off by glass I have used a similar tube, "end on," having a quartz window at one end.

The pressure of argon giving the greatest luminosity and most brilliant spectrum is three mm. At this point the color of the discharge is an orange-red, and the spectrum is rich in red rays, two being especially prominent at wave-lengths 696.56 and 705.64. On passing the current the traces of nitrogen bands soon disappear, and the argon spectrum is seen in a state of purity. At this pressure the platinum from the poles spatters over the glass of the bulbs, owing to what I have called "electrical evaporation,"[1] and I think the residual nitrogen is absorbed by the finely-divided metal. Similar absorptions are frequently noticed by those who work much with vacuum tubes.

If the pressure is further reduced, and a Leyden jar intercalated in the

[1] *Roy. Soc. Proc.*, 1, 88, June, *1891*.

circuit, the color of the luminous discharge changes from red to a rich steel blue, and the spectrum shows an almost entirely different set of lines. It is not easy to obtain the blue color and spectrum entirely free from the red. The red is easily got by using a large coil[1] actuated with a current of three amperes and six volts. There is then no tendency for it to burn blue.

The blue color may be obtained with the large coil by actuating it with a current of 3.84 amperes and eleven volts, intercalating a jar of fifty square inches surface. The make-and-break must be screwed up so as to vibrate as rapidly as possible. The red glow is produced by the positive spark, and the blue by the negative spark.

I have taken photographs of the two spectra of argon partly superposed. In this way their dissimilarity is readily seen.[2] In the spectrum of the blue glow I have counted 119 lines, and in that of the red glow eighty lines, making 199 lines in all; of these, twenty-six appear to be common to both spectra.

I have said that the residual nitrogen is removed by sparking the tube for some time when platinum terminals are sealed in. This is not the only way of purifying the argon. By the kindness of Professor Ramsay I was allowed to take some vacuum tubes to his laboratory and there exhaust and fill them with some of his purest argon. On this occasion I simultaneously filled, exhausted, and sealed off two Plücker tubes, one having platinum and the other aluminum terminals. On testing the gas immediately after they were sealed off, each tube showed the argon spectrum, contaminated by a trace of nitrogen bands. The next day the tube with platinum terminals was unchanged, but that having aluminum terminals showed the pure spectrum of argon, the faint nitrogen bands having entirely disappeared during the night. After an hour's sparking and a few days' rest the tube with platinum terminals likewise gave a pure argon spectrum. When a mixture of argon with a very little nitrogen is sparked in a tube made of pure fused quartz, without inside metallic terminals, the nitrogen bands do not disappear from the argon spectrum, but the spectra of argon and nitrogen continue to be seen simultaneously.

A vacuum tube was filled with pure argon and kept on the pump while observations were made on the spectrum of the gas as exhaustion proceeded. The large coil was used with a current of 8.84 amperes and eleven volts; no jar was interposed. At a pressure of three mm. the spectrum was that of the pure red glow. This persisted as the exhaustion rose, until at a pressure of about half a millimeter flashes of blue light made their appearance. At a quarter of a millimeter the color of the ignited gas was pure blue, and the spectrum showed no trace of the red glow.

[1] The coil used has about sixty miles of secondary wire, and when fully charged gives a torrent of sparks twenty-four inches long. The smaller coil gives six-inch sparks when worked with six half-pint Grove cells.

[2] Photographs of the different spectra of argon, and other gaseous spectra for comparison, were projected on the screen.

An experiment was now made to see if the small quantity of argon normally present in the atmosphere could be detected without previous concentration. Nitrogen was prepared from the atmosphere by burning phosphorus, and was purified in the usual manner. This gas, well dried over phosphoric anhydride, was passed into a vacuum tube, the air washed out by two fillings and exhaustions, and the tube was finally sealed off at a pressure of fifty-two mm. It was used for photographing the band spectrum of nitrogen on several occasions, and altogether it was exposed to the induction current from the large coil for eight hours before any change was noticed. The last time when photographing its spectrum difficulty was experienced in getting the spark to pass, so I increased the current and intercalated a small jar. The color immediately changed from the reddish yellow of nitrogen to the blue of argon, and on applying the spectroscope the lines of argon shone out with scarcely any admixture of nitrogen bands. With great difficulty and by employing a very small jar I was able to take one photograph of its spectrum and compare it with the spectrum of argon from Professor Ramsay, both being taken on the same plate, but the tube soon became non-conducting, and I could not then force a spark through, except by employing a dangerously large current. Whenever a flash passed it was of a deep blue color. Assuming that the atmosphere contains one per cent. of argon, the three mm. of nitrogen originally in the tube would contain 0.03 mm. of argon. After the nitrogen had been absorbed by the spattered platinum, this pressure of argon would be near the point of non-conduction.

In all cases when argon has been obtained in this manner the spectrum has been that of the blue-glowing gas. Very little of the red rays can be seen. The change from red to blue is chiefly dependent on the strength and heat of the spark : partly also on the degree of exhaustion. It is not improbable, and I understand that independent observations have already led the discoverers to the same conclusion—that the gas argon is not a simple body, but is a mixture of at least two elements, one of which glows red and the other blue, each having its distinctive spectrum. The theory that it is a simple body, has, however, support from the analogy of other gases. Thus, nitrogen has two distinct spectra, one or the other being produced by varying the pressure and intensity of the spark. I have made vacuum tubes containing rarefied nitrogen which show either the fluted band or the sharp line spectrum by simply turning the screw of the make-and-break, exactly as the two spectra of argon can be changed from one to the other.

I have prepared tubes containing other gases as well as nitrogen at different pressures, and have examined their spectra both by eye observation and by photography. The sharp line spectrum of nitrogen is not nearly so striking in brilliancy, number, or sharpness of lines as are those of argon, and careful scrutiny fails to show more than one or two apparent coincidences between lines in the two spectra. Between the spectra of argon and the band spectrum of nitrogen there are two or three close

approximations of lines, but a projection on the screen of a magnified image of the two spectra partly superposed will show that two at least of these are not real coincidences.

I have looked for indications of lines in the argon spectra corresponding to the corona line at wave-length 531.7, the aurora line at 557.1, and the helium line at 587.5, but have failed to detect any line of argon sufficiently near these positions to fall within the limits of experimental error.

I have found no other spectrum-giving gas or vapor yield spectra at all like those of argon, and the apparent coincidences in some of the lines which, on one or two occasions are noticed, have been very few, and would probably disappear on using a higher dispersion. As far, therefore, as spectrum work can decide, the verdict must be that Lord Rayleigh and Professor Ramsay have added one, if not two members to the family of elementary bodies.

The Liquefaction and Solidification of Argon. By Dr. K. Olszewski, Professor of Chemistry in the University of Cracow.

Having been furnished, by Professor Ramsay's kindness, with a sample of the new gas, argon, I have carried out experiments on its behavior at a low temperature and at high pressures, in order to contribute, at least in part, to the knowledge of the properties of this interesting body.

The argon sent by Professor Ramsay amounted to 300 cc. It was contained in a hermetically sealed glass bulb, so constructed that it could easily be transferred, with no appreciable loss, into the carefully dried and vacuous apparatus in which the proposed experiments were to be performed. The argon with which I was supplied, had, according to Professor Ramsay's statement, been dried with phosphoric anhydride; its density was 19.9 (H = 1); and he thought that at the outside it might contain one to two per cent. of nitrogen, although it showed no nitrogen spectrum when examined in a Plücker's tube.

Four series of experiments in all were carried out, two with the object of determining the critical temperature and pressure of argon, as well as measuring its vapor pressure at several other low temperatures, while two other series served to determine its boiling and freezing-points under atmospheric pressure, as well as its density at its boiling-point.

A detailed description of these experiments will be given in another place; I shall here give only a short description of the manner in which they were made.

For the first two experiments I made use of a Cailletet's apparatus. Its metallic manometer had been previously compared with the readings of a mercury manometer. As a cooling agent I used liquid ethylene, boiling under diminished pressure. The glass tube of Cailletet's apparatus was so arranged that the portion immersed in the liquid ethylene had comparatively thin walls (not exceeding one mm.), so as to equalize the external and internal temperature as quickly as possible.

In both the other experiments the argon was contained in a burette, closed at both ends with glass stop-cocks. By connecting the lower end

of the burette with a mercury reservoir, the argon was transferred into a narrow glass tube fused at its lower end to the upper end of the burette, and in which the argon was liquefied, and its volume in the liquid state measured. In these two series of experiments liquid oxygen, boiling under atmospheric or under diminished pressure, was employed as a cooling agent. I made use of a hydrogen thermometer in all these experiments to measure low temperatures.

Determination of the Critical Constants of Argon.

As soon as the temperature of liquid ethylene had been lowered to —128.6°, the argon easily condensed to a colorless liquid under a pressure of thirty-eight atmospheres. On slowly raising the temperature of the ethylene, the meniscus of the liquid argon became less and less distinct, and finally vanished at the following temperatures and corresponding pressures:

Expt.	Temperature.	Pressure.
1.	—121.2°	50.6 atmos.
2.	—121.6°	50.6 "
3.	—120.5°	50.6 "
4.	—121.3°	50.6 "
5.	—121.4°	50.6 "
6.	—119.8°	50.6 "
7.	—121.3°	50.6 "

In all seven determinations the critical pressure was found to be 506. atmospheres; but determinations of the critical temperature show slight differences. In experiments Nos. 3 and 6 less liquid argon was present in the tube than in the other five; in these the volume of liquid exceeded the volume of gas.

In determining the vapor pressures of argon, a tabular record of which is given below, I noticed slight differences of pressure according as I produced more or less of the liquid at the same temperature.

This proved that the sample of argon contained an inconsiderable admixture of another gas, more difficult to liquefy; it is doubtless the trace of nitrogen previously referred to. The mean of the seven estimations of the critical temperature is —121°, and this may be taken as the critical temperature of argon.

At lower temperatures the following vapor pressures were recorded:

Expt.	Temperature.	Pressure.
8.	—128.6°	38.0 atmos.
9.	—129.6°	35.8 "
10.	—129.4°	35.0 "
11.	—129.3°	35.8 "
12.	—129.6°	35.8 "
13.	—134.4°	29.8 "
14.	—135.1°	29.0 "
15.	—136.2°	27.3 "
16.	—138.3°	25.3 "
17.	—139.1°	23.7 "

In Experiments Nos. 9, 10, and 17, the quantity of liquefied argon was very small, for it filled the tube only to a height of three to five mm., and in the other experiments the column of liquid argon was twenty mm. high or more.

Determination of the Boiling and Freezing-Points.

Two hundred cc. of liquid oxygen, prepared in my large apparatus,[1] was poured into a glass vessel with quadruple walls, so as to isolate the liquid from external heat. After the liquid oxygen had been thus poured under atmospheric pressure, a great part of it evaporated, but there still remained about seventy cc., boiling under atmospheric pressure. A calibrated tube, intended to receive the argon to be liquefied, and the hydrogen thermometer were immersed in the boiling oxygen. At this temperature (—182.7°[2]) on admitting argon, no appearance of liquefaction could be noticed, even when compressed by adding a quarter of an atmosphere pressure to that of the atmosphere. This shows that its boiling-point lies below that of oxygen. But on diminishing the temperature of the liquid oxygen below —187° the liquefaction of argon became manifest. When liquefaction had taken place I carefully equalized the pressure of the argon with that of the atmosphere, and regulated the temperature, so that the state of balance was maintained for a long time. This process gives the boiling-point of argon under atmospheric pressure. Four experiments gave the numbers —186.7°, —186.8°, —187.0°, and —187.3°. The mean is —186.9°, which I consider to be the boiling-point under atmospheric pressure (740.5 mm.).

The quantity of argon used for these experiments, reduced to normal temperature and pressure was 95.5 cc.; the quantity of liquid corresponding to that volume of gas was approximately 0.114 cc. Hence the density of argon at its boiling-point may be taken as approximately 1.5. Two other determinations of the density of liquid argon, for which I employed still smaller quantities of the gas, yielded rather smaller numbers. Owing to the small amount of argon used for these experiments, the numbers given can not lay claim to great exactness; yet they prove that the density of liquid argon at its boiling-point (—187°) is much higher than that of oxygen, which I have found under similar conditions, to be 1.124.

By lowering the temperature of the oxygen to —191° by slow exhaustion, the argon froze to a crystalline mass, resembling ice; on further lowering temperature it became white and opaque. When the temperature was raised it melted; four observations which I made to determine its melting-point gave the numbers: —189.0°, —190.6°, —189.6°, and

1 *Bulletin International de l'Academie de Cracovie*, June, *1890;* also Wiedemann's *Beiblätter*, 15, p. 29.

2 I have redetermined the boiling-point of oxygen, using large quantities of oxygen, and a hydrogen thermometer of much larger dimensions than previously. The registered temperature is 1.3° lower than that which I previously recorded.

—189.4°. The mean of these numbers is —189.6°; and this may be accepted as the melting-point of argon.

In the table below I have given a comparison of physical constants, in which those of argon are compared with those of other so-called permanent gases. The data are from my previous work on the subject.

As can be seen from the appended table, argon belongs to the so-called "permanent" gases, and, as regards difficulty in liquefying it, it occupies the fourth place; *viz.*, between carbon monoxide and oxygen. Its behavior on liquefaction places it nearest to oxygen, but it differs entirely from oxygen in being solidifiable; as is well known, oxygen has not yet been made to assume a solid state.

Name.	Critical temperature.	Critical pressure.	Boiling-point.	Freezing-point.	Freezing pressure.	Density of gas.	Density of liquid at boiling-point.	Color of liquid
	Below.	Atmos.			mm.			
Hydrogen (H_2).....	—220.0°	20.0	?	?	?	1.0	?	Colorless
Nitrogen (N_2).....	—146.0°	35.0	—194.4°	—214.0°	60	14.0	0.885	"
Carbonic oxide (CO)..	—139.5°	35.5	—190.0°	—207.0°	100	14.0	?	"
Argon (A_1).....	—121.0°	50.6	—187.0°	—189.6°	?	19.9	Abt. 1.5	"
Oxygen (O_2).....	—118.8°	50.8	—182.7°	?	?	16.0	1.124	Bluish.
Nitric oxide (NO).....	— 93.5°	71.2	—153.6°	—167.0°	138	15.0	?	Colorless
Methane (CH_4).....	— 81.8°	54.9	—164.0°	—185.8°	80	8.0	0.415	"

The high density of argon rendered it probable that its liquefaction would take place at a higher temperature than that at which oxygen liquefies. Its unexpectedly low critical temperature and boiling-point seem to have some relation to its unexpectedly simple molecular constitution.

Professor Ramsay exhibited two sealed glass tubes which, he said, contained argon, and handed them round. He said that he had been asked by some of his friends to show them the gas. It was, however, quite invisible.

The President (Lord Kelvin).—It will be a satisfaction, I am sure, to anyone present to have one of these tubes in his hand, and to have really handled a glass vessel containing argon.

Dr. Armstrong (President of the Chemical Society).—I am sure, sir, I can say at once that all present to-day who are able to judge of a communication of this kind, and all others outside, will gladly join in the chorus which Mr. Crookes has proposed should be sung. But I should like, speaking more on behalf of the chemists—and I am sure that Professor Ramsay will come over to me for the time and dissociate himself from his colleague—to say that we feel especially indebted on this occasion to Lord Rayleigh, not only on account of the extraordinarily important information which he has placed at our disposal, but more particularly on account of the example which he has set us. You, sir, very

fully alluded in your address this year to the patient manner in which Lord Rayleigh had tracked this new element to its home. I feel sure that the words which fell from you will meet with the warmest approbation everywhere where such work can be understood. (Applause.) The case contained in the paper is undoubtedly a very strong one. Of course, in the hurry of a meeting like this, it has not been so logically brought forward by the reader of the abstract as it might have been, in order to do it full justice; but yet I think it will be quite clear to all who have listened to him that there is a very strong body of evidence which makes it certain that there is in the atmosphere a constituent which has long been overlooked, and a constituent having most extraordinary properties. The paper is not one which, so far as the experimental facts are concerned, can be criticised here. No doubt it will meet with very considerable criticism throughout the world. People will not be satisfied to take all these statements for granted without checking them, and I have not the least doubt that very soon we shall have abundant confirmations of the correctness of the discovery. But, apart from the facts which are brought forward in this paper, there is a portion which is purely—one almost might say, if I may be allowed the expression on such an occasion—of a wildly speculative character; that is the portion dealing with the probable nature of this new element. Professor Ramsay, in his remarks, in a measure let the cat out of the bag in a way which is not apparent when you read the paper, because it is quite clear that, after all, the authors of this communication are not so entirely satisfied with the evidence to be adduced from the application of the Clausius method for the determination of the atomicity of the gas. I think that they have not sufficiently taken into account, in dealing with this evidence, the extraordinary property that this gas possesses. Nitrogen we know is a very inert form of matter, but we know that the character of nitrogen derived from its study in the atmosphere is of an altogether wrong character. We know perfectly well that, taken as an element and treated as an atom, nitrogen is probably one of the most active forms of matter known to us, and that the great difficulty we have in bringing about its association with fresh elements, when we deal with that gas, arises from its extreme activity—its extreme fondness for its own self. Now, if we can judge anything at all from the properties which we know belong to this new element, it is, I imagine, that it is like nitrogen, but "much more so." It is quite conceivable that the condition which Professor Ramsay pointed out as being the only alternative to the one which is apparently accepted by the authors of the communication is a conceivable condition. It is quite likely that the two atoms exist so firmly locked in each other's embrace that there is no possibility for them to take notice of anything outside, and that they are perfectly content to roll on together without taking up any of the energy that is put into the molecule. There is a great deal to justify a view of this kind. Of course, it can not be discussed independently of what has been said with regard to the new gas

being a mixture; but it is quite clear that, as the discussion has gone on, the statements made in the paper are not so thoroughly accepted as one would think that they were. Mr. Crookes evidently wavers very much on this point with regard to there being two elements present, and I gather as much from Professor Ramsay's account. If we think that we are dealing with two gases here on the evidence of the spectroscope, there is no reason why we should not come to the same conclusion with regard to nitrogen and hydrogen. Oxygen, I believe, has three or four spectra, so that the spectroscopic evidence, after all, although it may be in a measure remarkable, does not appear to justify such a conclusion. The great difficulty that we have, I take it, in accepting the conclusion that we are dealing with an element having a molecular weight of forty, and an atomic weight of forty, arises from the difficulty of placing an element of that kind, which practically seems to me to have driven the authors to the conclusion that, possibly, they are dealing with a mixture. The difficulty would be got over, of course, if we were dealing with a complex body, and I think that was rather hinted at by Professor Ramsay when he referred to one of Olszewski's numbers. This low value, high as it is in comparison with that of nitrogen obtained from the density of the liquid, is a reason which would induce us to place it higher up in the scale of elements, and give it a lower weight. Of course, these are all matters which must be discussed later on more fully; they are matters which can only be discussed very gradually, as we learn more about this substance. As regards its inactivity, very possibly that may be exaggerated. It is very difficult, in a case like this, to find out what are the best conditions to make use of. We know perfectly well that, if we were not in possession of the electric spark, we could scarcely have discovered that nitrogen might be combined with hydrogen to form ammonia direct. We know that we can only bring about the combination of the two if we are in a position at once to remove the product; and that sort of thing may well obtain in a case like this. We know very well that there are comparatively few substances which can be directly associated with nitrogen. It is quite likely that here we are dealing with an element which has still fewer affinities, but it does not follow by any means yet—nor do the authors assert such to be the case—that we are dealing with an element which is entirely inactive even in the form in which it is presented to us. This is not the occasion to discuss the matter fully, but these are points which certainly deserve consideration, and they are some of the first points which make this element of such importance and interest to us as chemists. In conclusion, I can only heartily congratulate the authors on having given us this communication.

Professor Rücker (President of the Physical Society).—I think it is very important on this occasion that we should remember that this is a discussion meeting of the Royal Society, a meeting held in this way for the first time, and a meeting at which reporters are present in order that the net result of the discussion shall go out at once to the world. It is, there-

fore, I think, extremely important that we should distinguish as clearly as possible between the various points of doubt which still may remain with regard to the new element which has been described to-day, and the one certain fact which comes out indisputably from the facts which have been laid before us; namely, that in spite of the doubt which may have existed on the matter for the last few weeks or months, we have it now beyond all question—and I quote the words of the President of the Chemical Society in saying so—that it is certain that we have here a new constituent of the atmosphere. What the importance of this is has already been mentioned, and I want once more to emphasize the fact that this central feature stands out quite clear, apart from whether we have one or two, and apart altogether from whether the various physical quantities which have been laid before us to-day have been measured with the accuracy which may be obtained in the future. But there is one particular point to which I should like to refer. It seems to me that one of the most interesting results arrived at from the physical point of view is the fact that the gas is monatomic. Some of us have had the opportunity of seeing the paper before it was read to-day, and we are therefore, perhaps, aware of one or two facts which, I think, were not actually mentioned by Professor Ramsay. One of these facts is that the experiments required to determine the ratio of the two specific heats were made twice over, or many times over, for all I know, but made in two different ways. They were made in a narrow tube, and they were made in a wide tube; and further check experiments were carried on in which other gases were compared with the new element. There can be no possibility of doubt as to a result of this sort when the experiments are carried out by two such men as Lord Rayleigh and Professor Ramsay. The matter is one which admits of no mistake when conducted in this way, and it must be accepted as certain that the element has that particular ratio of specific heats. Well, then the question arises, What follows from this? I think that it has not perhaps, been quite sufficiently pointed out that, in order that this ratio may be obtained if we are to use the ordinary mechanical theory of gases, it is necessary that the atom with which we are dealing should be regarded as spherical. Of course, I am well aware that our pictures of spherical and the like are, no doubt, only approximations to the truth; but if we are to conceive this atom as consisting of two which are closely united, the one with the other, we must nevertheless suppose, from that point of view, that they are so united as to form a sphere. That is only one way of putting it, but, nevertheless, it does create a difficulty which, I think, has not been altogether referred to before, I can only, in conclusion, say that, whatever the effect may be upon the great chemical generalization of Mendelejeff, that is, after all, an empirical law which is based, at present, upon no dynamical foundation. If it holds its own in this case, it will, of course, strengthen our belief in it, but, on the other hand, I do not think that it stands on the footing of those great

mechanical generalizations which could not be upset without upsetting the whole of our fundamental notions of science.

The President.—Among those present I am sure those who understand most of the subject will be anxious to speak. I now ask any person present to make remarks, and especially to ask questions.

Professor Roberts-Austen.—I should like to say that, when this beautiful discovery was communicated to the British Association, I ventured to point out that it was not too soon to consider its relation to the great metallurgical industries in which air is largely employed. In the Bessemer process alone you take some ten tons of iron and put it into a vessel called a converter. It is melted, and air is passed through to remove the carbon, silicon, phosphorus, and other impurities. That means that no less than 100,000 cubic feet of air pass through the metal. Therefore, 1,000 cubic feet of argon have gone somewhere. Now, I have taken Bessemer-blown metal, which has been treated with ferro-manganese, and have pumped out forty times its volume of gas, of which one-twentieth was nitrogen. In that nitrogen I have not been able to detect any argon that could not have come from the water which was necessarily used in the manipulation. I have taken a small quantity of air and abstracted argon from it, and obtained exactly the proportion that the authors say it contains, so I am perfectly certain that the manipulation is correct. But it remains to be seen whether the argon finds its way into the iron, as nitrogen undoubtedly does, and, if it does, whether it stays there, because there are certain peculiarities that make Bessemer metal different from other kinds of steel, and it would be most interesting if we could succeed in tracing it to some of this 1,000 cubic feet of argon which has either passed into the air or into the iron. I should just like to say that I could have wished that the authors of the paper had dialyzed the air through india-rubber, and not have merely used clay pipes. As one so long associated with Graham, I can only say how delighted he would have been had he known that his method would have been used by the authors of this paper, one of whom occupies Graham's own chair at University College.

Lord Rayleigh.—I have very little to add to the account which my colleague, Professor Ramsay, has given of this research. The research has been, in many respects, a very difficult one. I am not without experience of experimental difficulties, but certainly I have never encountered them in anything like so severe and aggravating a form as in this investigation. Every experiment that one attempts takes about ten days or a fortnight to carry out to any definite conclusion, and the result has been, of necessity, much less progress than we could have hoped for, and many of the questions have been left open which we could have wished to settle. One such question has just been alluded to by Professor Roberts-Austen; namely, the character of the gas transfused through india-rubber. That experiment has been upon our program, I may almost say from the first, but hitherto time has not been found to carry it out. The

difficulties of those parts of the research with which I have been more particularly connected have been very great. The preparation of the gas in sufficient quantity to experiment with at all has been no easy matter, and some of the results, such as those relating to the density of the gas, are consequently not so satisfactory and not so thoroughly elaborated as one could have wished. One point that has been mentioned relates to the argument in favor of the monatomicity of the gas. Of course, what is directly proved by the experiment, if it is good, is that the whole, or nearly the whole, of the energy put into the gas, when it is heated, is devoted to increasing the energy of its translatory motion, and that no margin remains over, as in the case of other gases, to be attributed to intermolecular or interatomic motion. At first sight it seems rather a strange thing that there should be no rotation in the molecules of the gas. How can it be? Can they be without rotation, or can the energy of their rotation be so small as to be negligible in comparison with the energy of the motion as a whole? That is a difficulty which I think has not been thoroughly met hitherto by the cultivators of the dynamical theory of gases; but apparently here we may accept it that no such energy exists, or that no such energy exists in any appreciable degree. Of course, that condition is quite well met by the suggestion which has been put forward, and which has also been communicated to us by Professor Fitzgerald, of Dublin, who writes as follows:

"The reason why the ratio of specific heats of 1.66 is supposed to prove monatomicity in a gas is because in a monatomic gas there are no internal motions of any consequence. Now, if the atoms in a molecule are so bound together that hardly any internal motions exist, it would, so far as specific heat is concerned, behave like a monatomic element. That the atoms in argon may be very closely connected seems likely from its very great chemical inertness. Hence, the conclusion from the ratio of its specific heats may be, not that it is monatomic, but that its atoms are so bound together in its molecule that the molecule behaves, as a whole, as if it were monatomic."

That argument is, no doubt, perfectly sound, but the difficulty remains how you can imagine two molecules joined together, which one figures roughly in the mind, and I suppose not wholly inaccurately, as somewhat like two spheres put together and touching one another—how it would be possible for such an excentrically-shaped atom as that to move about without acquiring a considerable energy of rotation. That is difficult, and I think the only interpretation is, that the gas is monatomic. No doubt the whole subject is one about which we know exceedingly little, mercury vapor being the only other gas at present which exhibits a similar property. I am not sure that any other point has been raised, but if any questions are asked, Professor Ramsay and myself are quite ready to give further explanations, so far as it is in our power to do so.

The President.—I wish to make a remark, not as from the chair, but with reference to the question which is now before us, as to the condition

under which the ratio of the specific heats could be exactly one and two-thirds. I do not admit that a spherical atom could fulfill that condition. A spherical atom would not be absolutely smooth. In other words, it must be a Boscovitch point. Neither can I admit that excessively rigid connection between two atoms could give it the quality of having no capacity whatever for a relative vibratory movement. It would need infinitely stiff connections to give it no capacity for relative vibratory movement; and if it had infinitely stiff relative connection the connection of the two bodies would be indissoluble, and they would remain one. In fact, I think that the only kind of atom that we can conceive as giving, in the dynamical theory of heat, rigorously the ratio of one and two-thirds for the specific heat is the ideal Boscovitch mathematical point endowed with the property of inertia, and with the other property of acting upon neighboring points with a force depending upon distance. I have now to ask for any further remarks. I do not wish to close this most interesting discussion. I hope we shall have further discussion and further questions.

If there are no more remarks and no questions to be put, I desire now, in the name of the Royal Society, to thank the Senate of the University of London for their hospitality on this occasion, a hospitality which I am sure we have all very much enjoyed. I have great pleasure in joining with the President of the Chemical Society, and the President of the Physical Society in congratulating Lord Rayleigh and Professor Ramsay on the brilliant success already obtained. (Great cheering.) I join with my brother Presidents in wishing them more and more success in the continuation of their work, and in thanking them heartily in the name of the Royal Society for the communication which they have given us this day. (Cheers.)

Calcium Sulphite Stalactites and Stalagmites.—Under a number of large wooden tanks, in which "Bisulphite of Lime," of the trade, has been stored for a year or more, a curious stalactitic formation was observed.

The "Bi-sulphite of Lime," seeping through minute openings in the bottoms of the tanks, had been precipitated as calcium sulphite by the evaporation of free sulphurous acid, in a manner perfectly analogous to the natural formation of stalactitic deposits of calcium carbonate.

The stalactites examined were from six to eighteen inches in length, generally with a small hole vertically through the center, granular in structure, more or less stained with iron, and partially oxidized to calcium sulphate. A few were made up of concentric rings of granular crystals, alternate rings being more deeply stained with iron. One specimen, radiately fibrous in

structure, was beautifully crystallized. The stalactites were usually irregular cones with the altitude from five to ten times the diameter of the base.

In many cases the stalactite and stalagmite had become united forming an irregular cylindrical column.

The stalagmites examined were all granular in structure and usually less deeply stained than the corresponding stalactites. One specimen was white and very well crystallized. Like the stalactites they were usually more or less oxidized. The vertical axis was shorter, in proportion to the diameter of the base, and the apex more rounded, than in case of the stalactites.

The phenomenon is deserving of attention as an illustration of the well-known analogy between the sulphites and carbonates of the alkaline earth metals, as regards insolubility in water, but ready solubility in water containing sulphurous or carbon dioxide respectively. It is also interesting as showing a further analogy between two classes of salts which do not fall in the same period in the Mendelejeff classification.

DAVID HANCOCK.

CUMBERLAND, MD., January 18, 1895.

NEW BOOKS.

A TEXT-BOOK OF INORGANIC CHEMISTY. DESCRIPTIVE, THEORETICAL, AND PRACTICAL. A MANUAL FOR ADVANCED STUDENTS. BY ALFRED A. BENNETT, PROFESSOR OF CHEMISTRY IN THE IOWA COLLEGE OF SCIENCE, AGRICULTURE, AND THE MECHANIC ARTS. 2 Vols., 12 mo. 11 Illustrations. New York, Boston, Chicago: Silver, Burdette & Co. 1892 and 1894. Introductory price, $1.50 per volume.

It has lately been stated in a book review in these pages that there is doubtful room for new text-books on inorganic chemistry; and, in view of the important number of standard works of acknowledged value and usefulness extant, most instructors will heartily concur in this view. Every teacher, however, has his own ideas of how best to present the subject to his students to enable them to readily and intelligently grasp it, and whatever may be the text-book employed, it can in any case be followed only as a general guide and be adapted to the needs and conditions in each case. The work before us may fairly claim to be of such general adaptability as to be useful in most cases, and

particularly in those in which objective teaching, now properly so prevalent, has been adopted. It is essentially a laboratory guide rather than a lecture adjuvant, a manual rather than text-book, and its aim is to furnish such schemes for practical work with chemicals and apparatus in the hands of students as will lead them by actual practice and observation to grasp the fundamental principles of the science, describing the properties of the elements and compounds little further than is necessary to the development of these principles or to emphasize the facts that should be gleaned from observation and experiment.

The first volume (pp. 357) of the work is devoted to the so-called non-metallic elements, and after the usual brief discussion of matter and energy, the relations of physics and chemistry, and the conservation of matter and energy, begins with a study of hydrogen and the halogens and the combinations of the former with the latter. From the properties and reactions covered in this study are developed the hypotheses, theories, and laws which constitute, as it were, the axioms of chemistry. This general principle is followed throughout the work, and the facts concerning each element are studied in the following order: 1. Occurrence and distribution; 2. Methods of preparation; 3. Preparation; 4. Experimental study; 5. Physical properties; 6. Chemical properties; 7. Name, derivation, meaning, and symbol; 8. History; 9. Uses; 10. Special tests for recognition of the elements; 11. (For compounds.) The determination of molecular formulas. And along with this, theoretical considerations are developed in a logical manner.

Under the caption "Experimental Study" are offered directions for making experiments which, it is expected, will be explained to the class in the lecture room and will be carried out later in the laboratory by the students, who will likewise be required to keep copious notes of their operations and observations. Supplemental to these directions are offered certain arithmetical problems illustrative of the principle and properties developed, and unfinished equations which the student is directed to complete.

An interesting and novel feature of the book is the limited study of potassium and sodium in connection with, and imme-

diately following, that of the compounds of hydrogen, the halogens, and oxygen, thus "introduced in order that the learner may have some facts to use in the consideration of acids and bases."

The second volume (pp. 366) is devoted to the metallic elements, their properties, and reactions (pp. 299); the classification of the elements in accordance with the periodic law (pp. 18); a system of qualitative analysis, (pp. 47), concluding with a table of seventy-two elements with their atomic "masses," prepared by F. W. Clarke and a blank table of solubilities of salts to be filled by the student as he determines these properties in his experiments.

"Mass" is used in preference to weight and the system of spelling recommended by the committee of the American Association for the Advancement of Science followed throughout.

Having developed the significance of valence and atomic mass in the first volume, the author devotes considerable space in this volume, in connection with each metal, to the facts which determine its classification with regard to these properties; and in view of the difficulties which students frequently meet in acquiring familiarity with them, this provision will, in many cases, prove most valuable.

The volumes are, each of them, provided with excellently arranged indexes, are of such form and size as to be convenient for use either in the study, the lecture room, or the laboratory, and are offered in attractive style both as to binding and typography.

WM. MCMURTRIE.

QUALITATIVE CHEMICAL ANALYSIS OF INORGANIC SUBSTANCES AS PRACTICED IN GEORGETOWN COLLEGE, D. C. pp. 61. New York: American Book Company. 1894. Price $1.50.

This small book is divided into four parts: I. Basic Analysis. II. Acid Analysis. III. Preliminary Examination. IV. Solution of Solid Substances.

The bases are grouped and numbered according to Fresenius. The method of describing the properties and characteristic reactions of the elements of each group is somewhat different from that commonly used. A brief note of the properties of the element itself is first given, then the names and formulas of the

most common soluble compounds, and then the insoluble compounds under which head the characteristic reactions are given by first naming the insoluble compound or precipitate and then stating how it is formed, giving its properties, etc. Although the author states that "only these facts have been selected which are indispensable in a course such as the one for which the book is intended," it would seem that too large a number of characteristic reactions are either omitted or reserved to the analytical tables and explanations of the tables, and that in consequence the student hardly did a sufficient number of these important experiments before going on with a group separation.

This form of arrangement, however, may possess some advantages over the usual method of procedure. Certain it is that the explanations connected with each table of analysis is one of the best features of the book and bears evidence of careful and conscientious work on the part of the author. In treating of the acids the usual preliminary experiments upon the characteristic reactions of the individual acids of each group are entirely dispensed with, and instead one passes immediately to their separation and detection. To be sure the special tests applied to the separate portions of the original solution are characteristic. And the explanation of them is apt, still here again it would seem that some experience should be had in noting their deportment toward certain reagents befere going to their separation. The preliminary examination and the solution of substances is substantially the same as ordinarily given in most text-books.

W. J. KARSLAKE.

ADDENDUM.—Professor Mabery makes the following addition to his article in the February number, page 105, after the words "Morley determined with the utmost precision the proportions of oxygen without finding any appreciable variations," insert the following:

In certain conditions of the atmosphere, when a vertical descent of the upper portions occurs, Professor Morley observed a deficiency in oxygen equivalent to 0.16 per cent.